European
Commission

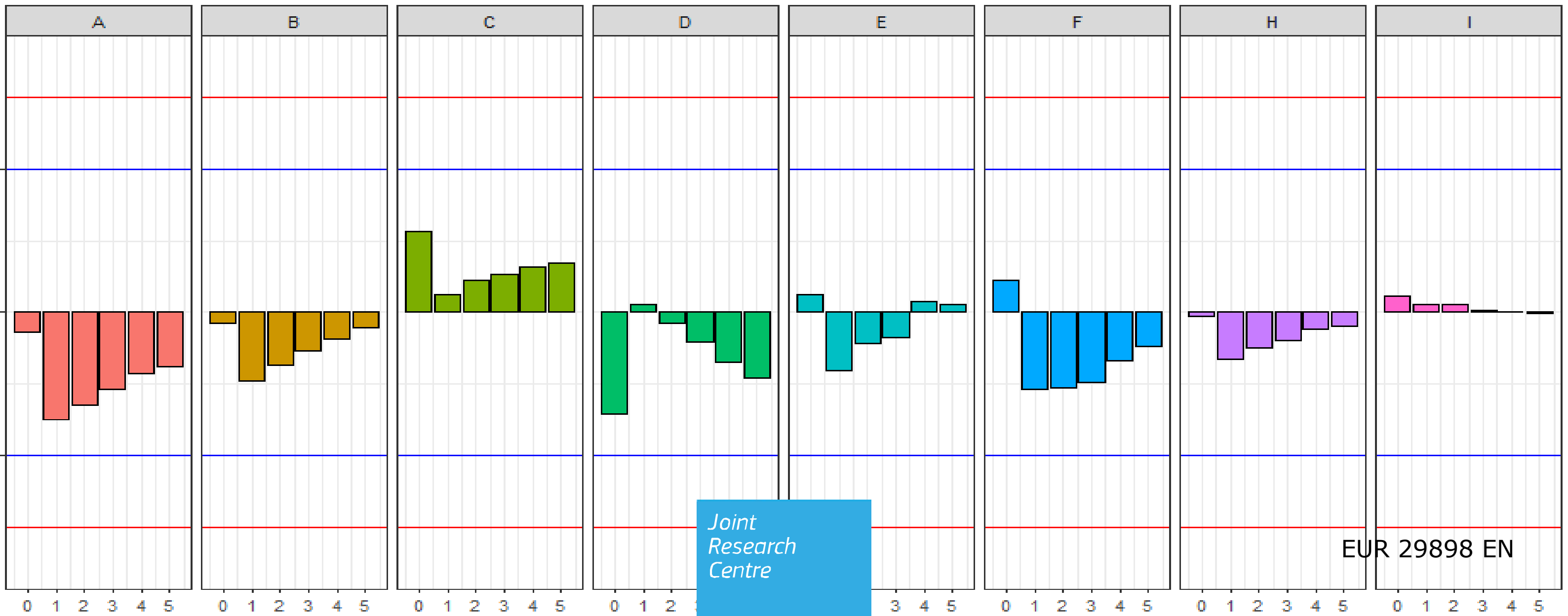
JRC TECHNICAL REPORT

Evaluation of the Inter-Laboratory Comparison exercise for SO_2, CO, O_3, NO and NO_2 (13-16 May 2019, Ispra)

European Commission harmonisation programme for air quality measurements

Barbiere M., Lagler F., Borowiak A.

2019



Joint
Research
Centre

EUR 29898 EN

Contact information
Name: Annette Borowiak
Address: European Commission, Joint Research Centre, Via E. Fermi 2749, 21027 Ispra (VA), Italy
Email: annette.borowiak@ec.europa.eu
Tel.: +39 0332 789956

EU Science Hub
https://ec.europa.eu/jrc

JRC118182

EUR 29898 EN

PDF ISBN 978-92-76-12334-7 ISSN 1831-9424 doi:10.2760/659833

Luxembourg: Publications Office of the European Union, 2019

How to cite this report: Barbiere M., Lagler F., Borowiak A., *Evaluation of the inter-laboratory comparison exercise for* SO_2*, CO,* O_3*, NO and* NO_2*, 13-16 of May 2019 Ispra, Italy - European Commission harmonisation programme for air quality measurements*, EUR 29898 EN, Publications Office of the European Union, Luxembourg, 2019, ISBN 978-92-76-12334-7, doi:10.2760/659833, JRC118182.

Table of contents

1. Acknowledgements

In collaboration with:

ADAMS Jan, BERNBERG Stephan, DE MIGUEL Jose Miguel, DELANEY Lin, DÉZSI Viktor, GURDEBEKE Pieter, JURCOVIC Maros, LENGYEL Jozef, LUSA Kaisa, NYGAARD Jesper, PÓLAY Gábor, REISENHOFER Michael, RUANE Cathal, SAARNIO Karri, SILLOVA Zuzana, SNELLSTRÖM Johanna, SORIANO RODRÍGUEZ María, WOLF Andreas.

	NAME	**VERSION**	**DATE**
Editing	A. BOROWIAK (Coordinator) F. LAGLER (Technician) M. BARBIERE (Technician/QO)	DRAFT	15/06/2019
Review	N. JENSEN (Scientist/QO)	DRAFT1	05/08/2019
Validation	E. VIGNATI (Head of Unit)	FINAL	10/10/2019
Approval	P. SZYMANSKI (Director)	FINAL	28/10/2019

2. Abstract

Within the harmonisation programme of Air Quality monitoring in Europe the European Reference Laboratory of Air Pollution (ERLAP) organises Inter-Laboratory Comparison exercises (ILC). From the 13th to the 16th of May 2019, including ERLAP, ten Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met for a laboratory comparison exercise in Ispra (IT) to evaluate their proficiency in the analysis of inorganic gaseous air pollutants (NO, NO_2, SO_2, CO and O_3) covered by the European Air Quality Directive 2008/50 EC [1] and its recent amendments 2015/1480/EC [42]. One laboratory reported only values for NOx and O_3.

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

On the basis of adopted criteria (z'-score), 86% of all results reported by AQUILA laboratories were satisfactory both in terms of measured values and reported uncertainties. The rest of the results had satisfactory measured values, but the reported uncertainties were either too high (8%) or too small (4%). The rest of the results consist in four values (2%) found to be questionable always for z'-score. During this ILC no unsatisfactory results were identified.

Comparability of results among AQUILA participants at the highest generated concentration levels is satisfactory for measurements of all pollutants.

3. Introduction

The Directive 2008/50/EC [1] on ambient air quality and cleaner air for Europe sets a framework for a harmonised air quality assessment in Europe.

One important objective of the Directive [1] is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O_3). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQOs) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods for CO [2], SO_2 [3], NO-NO_2 [4] and O_3 [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Air Quality Directive [1, 42], the European Reference Laboratory of Air Pollution (ERLAP) of the Directorate for Energy, Transport and Climate at the Joint Research Centre (JRC) organises inter-laboratory comparison exercises (ILC) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of the Member States of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 **[9] [10], [24], [31], [35], [38]** and **[45]** but with a view to obtaining harmonised air quality data for health related studies. Their programme integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimise resources and improve international harmonisation.

The following report deals with the ILC that took place from 13th to the 16th of May 2019 in Ispra (IT).

Since 1990 ERLAP has organised ILC in order to evaluate the comparability of measurements carried out by NRLs and promote information exchange among the expert laboratories. Recently, a more systematic approach has been adopted, in agreement with the Network of National Reference Laboratories for Air Quality (AQUILA) [11], aiming to both provide an alert mechanism for the purposes of the EC legislation and support the implementation of quality schemes by NRLs.

The methodology for the organisation of ILC was developed by ERLAP in collaboration with AQUILA and is described in a paper on the organisation of laboratory comparison exercises for gaseous air pollutants [12].

This evaluation scheme was adopted by AQUILA in December 2008 and is applied to all ILC since then. It contains common criteria to alert the EC on possible performance failures which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z'-score method [13] with the uncertainty requirements for calibration gases stated in the European standards [2], [3], [4] and [5], which are consistent with the DQOs of European Directives.

According to the above-mentioned document, NRLs with an overall unsatisfactory performance in the z'-score evaluation (one unsatisfactory or two questionable results per parameter) ought to repeat their participation in the following ILC in order to demonstrate remediation measures [12]. In addition, considering that the evaluation scheme should be useful to participants for accreditation according to ISO 17025, they are requested to include their measurement uncertainty. Hence, participants' results (measurement values and uncertainties) are compared to the assigned values applying the E_n–score method [13].

Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardised measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different ILC.

4. Inter-laboratory organisation

The ILC was announced in February 2019 to the members of the AQUILA network and the WHO CC representative. Registration was opened in April 2019 and closed at the beginning of May 2019.

Every participant, together with the registration confirmation, received a detailed protocol with all the necessary information about the ILC. Each laboratory was required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the ILC).

The participants were invited to arrive on Monday, 13th of May 2019, for the installation of their equipment. The calibration of NOx and O3 analysers was carried out next day on Tuesday morning and the generation of NOx and O3 gas mixtures started at 11:00.

The calibration of SO2 and CO analysers was carried out on Wednesday afternoon and the generation of CO and SO2 gas mixtures started at 20:00.

The test gases generation and measurements finished on Thursday at 9:00.

4.1 Participants

All participants were organisations dealing with the routine ambient air monitoring or institutions involved in environmental or public health protection. The national representatives came from Belgium, Denmark, Spain, Ireland, Hungary, Slovak Republic, Austria, Finland and Sweden.

Table 1: List of participating organizations.

Country	Laboratory	Code
Belgium	Flemish Environmental Agency	A
Denmark	National Environmental Research Institute	B
Spain	Instituto De Salud Carlos III	C
Ireland	Environmental Protection Agency	D
Hungary	Hungarian Meteorological Service	E
Slovak Republic	Slovak Hydro-meteorological Institute	F
European Commission	European Reference Laboratory for Air Pollution	G
Austria	Umweltbundesamt GmbH	H
Finland	Finnish Meteorological Institute	I
Sweden	Stockholm University ACES	K

Table 2 reports the manufacturer and model of the instrumentation used by every participant during the inter-laboratory comparison exercise including those used in the calculation of the assigned values.

The list contains the information reported by participants and cannot be considered as an implicit or explicit endorsement by the organisers of any specific instrumentation.

Table 2: List of instruments used by participants.

code	parameter	analyser
A	SO2	Thermo Scientific, 2010, 43i
B		Teledyne API T-100 SO2 monitor
C		Thermo 43i
D		API T100 2016
E		Thermo scientific 43i
F		Horiba, 2009, APSA-370
G		Thermo 43i, 2009
H		Thermo Env. Corp, TEI 43 C-TL, 1999
I		Thermo 43i TLE, 2012
K		/
A	NOx	Thermo Scientific, 2011, 42i
B		Teledyne API T-200
C		Thermo 42i
D		api, 2016, T200
E		Thermo Scientific 42i,
F		Horiba, 2010, APNA-370
G		Thermo, TE42iTL, 2015
H		Horiba, 2007, APNA 370
I		Horiba APNA-360, 2002
K		Enviroment, 2012, AC32M
A	CO	API, 2012, T300
B		Teledyne API T-300 CO monitor
C		Thermo 48i
D		API T300 2014
E		Thermo scientific 48i
F		Horiba, 2003, APMA-360
G		Horiba, APMA-370, 2010
H		Horiba, 1997, APMA 360 CE
I		Horiba APMA-360, 1999
K		/
A	O3	Thermo Scientific, 2009, 49i
B		Teledyne API T-400
C		Thermo 49i
D		API T400 2013
E		Thermo Scientific 49i
F		Horiba, 2006, APOA-360
G		Thermo, 49-iPS , 2015
H		Thermo Fisher Scientific TEI 49 i, 2013
I		Thermo 49i-B1NAA, 2012
K		Teledyne, 2004, API T400

4.2 Preparation of test mixtures

The ERLAP ILC facility has been described in several reports [17], [18]. During this ILC, gas mixtures were prepared for SO_2, CO, O_3, NO and NO_2 at concentration levels around limit values, critical levels and assessment thresholds set by the European Air Quality Directive [1].

Table 3: Sequence program of generated test gases with indicative pollutant concentrations

day	start time	duration	parameter	installation	calibration	Zero Air	NO	NO2	O3	CO	SO2
		h				nmol/mol	nmol/mol	nmol/mol	nmol/mol	mmol/mol	nmol/mol
1st	09:00		/	X							
2nd	08:00	3	/		X						
2nd	11:00	1	NO-NO_2-O_3			X					
2nd	12:00	2	NO-NO_2				135				
2nd	14:00	2	NO-NO_2				70	65			
2nd	16:00	2	O_3						65		
2nd	18:00	2	NO-NO_2				35				
2nd	20:00	2	NO-NO_2				15	20			
2nd	22:00	2	O_3						20		
3rd	00:00	2	NO-NO_2				65				
3rd	02:00	2	NO-NO_2				25	40			
3rd	04:00	2	O_3						35		
3rd	06:00	2	NO-NO_2				490				
3rd	08:00	2	NO-NO_2				380	110			
3rd	10:00	2	O_3						115		
3rd	12:00	2	NO-NO_2				300				
3rd	14:00	2	NO-NO_2				200	100			
3rd	16:00	2	O_3						90		
3rd	< 18:00	2	/		X						
3rd	20:00	1	CO-SO_2			X					
3rd	21:00	2	CO-SO_2							2.8	115
3rd	23:00	2	CO-SO_2							8.5	60
4th	01:00	1	CO-SO_2			X	not to be reported				
4th	02:00	2	CO-SO_2							5	35
4th	04:00	2	CO-SO_2							2	18
4th	06:00	2	CO-SO_2							0.9	10
4th	08:00	1	/								
4th	09:00	END									

The test mixtures were prepared by the dilution of gases from cylinders containing high concentrations of NO, SO_2 or CO using thermal mass flow controllers [8]. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration method [19] in a condition of NO excess.

The participants were required to report three half-hour-mean measurements for each concentration level (run) in order to evaluate the repeatability of standardised measurement methods. Zero value concentration levels were generated for one hour and one half-hour-mean measurement was reported. The sequence programme of generated test gases is given in Table 3.

5. The evaluation of laboratory's measurement proficiency

To evaluate the participant's measurement proficiency, the methodology described in ISO 13528 [13] was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole ILC [12].

The traceability of ERLAP's measurement results and the method applied to validate them are presented in paragraph 8. In the following proficiency evaluations, the uncertainty of test gas homogeneity (paragraph 8) was added to the uncertainties of ERLAP's measurement results.

All data reported by participating laboratories are presented in 0.

As described in the AQUILA document 37 [12], the proficiency of the participants was assessed by calculating two performance indicators.

The first performance indicator (z'-score) tests whether the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion.

The second performance indicator (E_n-score) tests if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participants measurement result and the uncertainty of the assigned/reference value.

5.1 z'–score

The z'- score statistic is calculated according to ISO 13528 [13] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_X^2}} \qquad \textbf{Equation 1}$$

where $\boldsymbol{x_i}$ is a participant's average value for each run, $\boldsymbol{X}$ is the assigned/reference value, $\boldsymbol{\sigma_p}$ is the standard deviation for proficiency assessment and $\boldsymbol{u_X}$ is the standard uncertainty of the assigned value. For ***a*** and ***b*** see Table 4.
In the European standards [2], [3], [4] and [5] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.
Over the whole measurement range σ_p is calculated by linear interpolation between 2.5% at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous ILC. The linear function parameters of σ_p are given in Table 4.

Table 4: Standard deviation for proficiency assessment (σ_p).

σ_p is a linear function of concentration (c) with parameters: slope (a) and intercept (b).

Gas	σ_p=a·c+b a	 b nmol/mol
SO_2	0.022	1
CO	0.024	100
O_3	0.020	1
NO	0.024	1
NO_2	0.020	1

The assessment of results in the z‘-score evaluation is made according to the following criteria:

- |z′| ≤2 are considered satisfactory.
- 2 < |z′| < 3 are considered questionable.
- |z′| ≥ 3 are considered unsatisfactory. Scores falling in this range are very unusual and are taken as evidence that an anomaly has occurred that should be investigated and corrected.

The results of z′-score evaluation are presented in bar plots (Figure 1 to 5) in which the z′-scores of each participant are grouped together. The assessment criteria are presented as z′=±2 (blue line) and z′=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

Figure 1: Z′-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (115 nmol/mol), 2 (60 nmol/mol), 3 (35 nmol/mol), 4 (18 nmol/mol), 5 (10 nmol/mol).

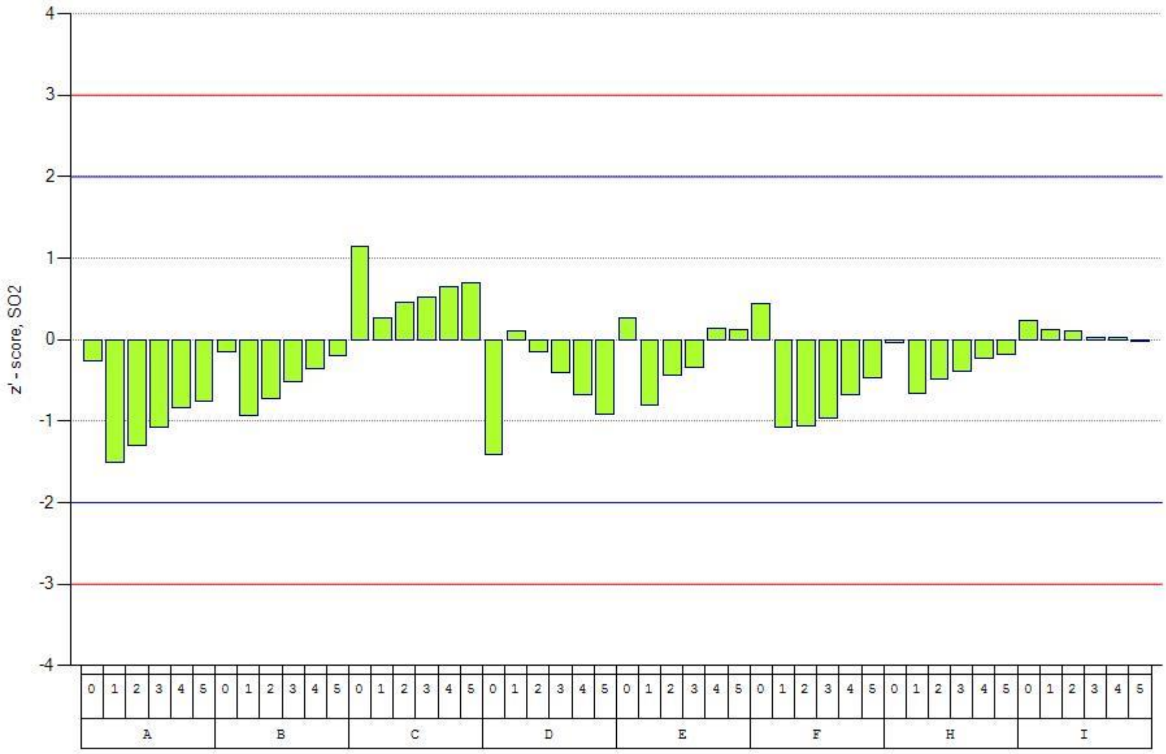


Figure 2: Z'-score evaluations of CO measurements

Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (2.8 µmol/mol), 2 (8.5 µmol/mol), 3 (5 µmol/mol), 4 (2 µmol/mol), 5 (0.9 µmol/mol).

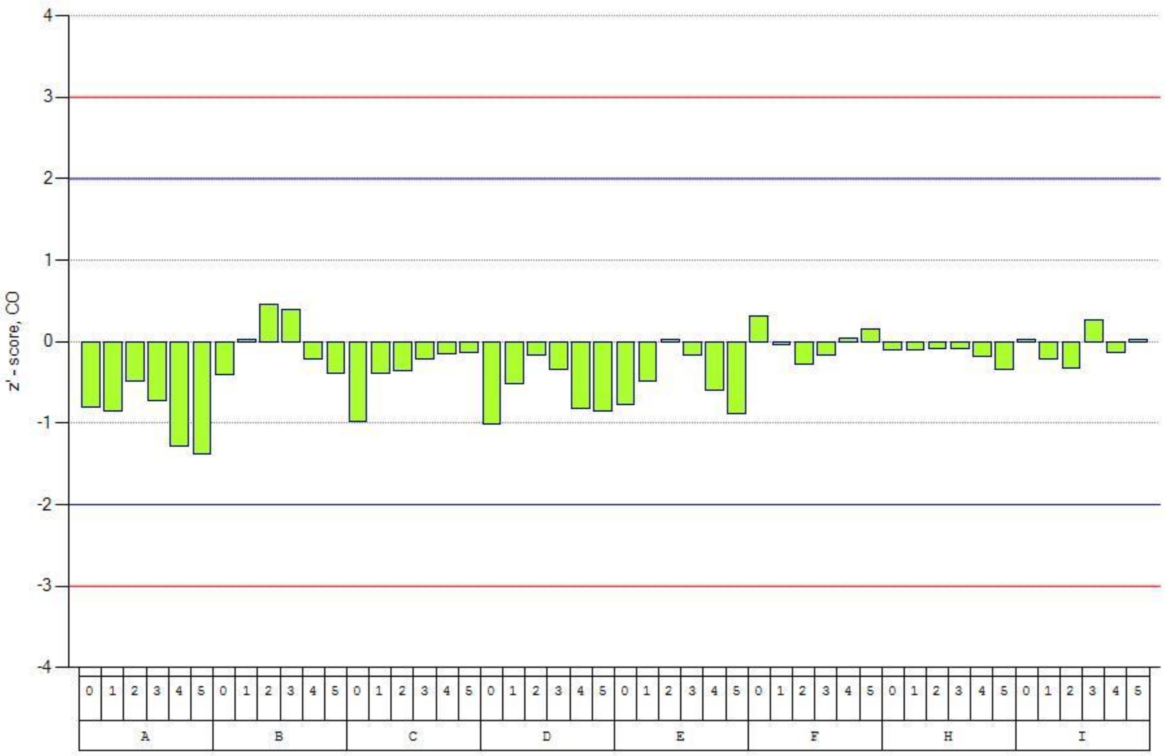


Figure 3: Z'-score evaluations of O_3 measurements

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (65 nmol/mol), 2 (20 nmol/mol), 3 (35 nmol/mol), 4 (115 nmol/mol), 5 (90 nmol/mol).

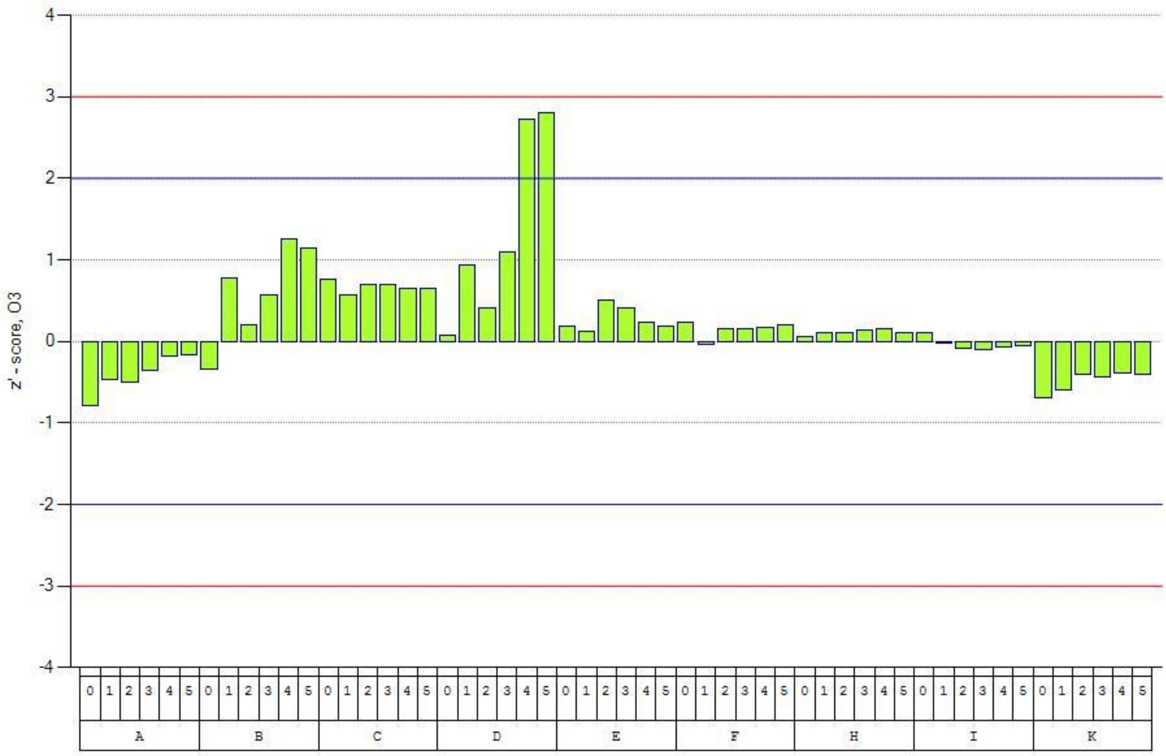


Figure 4: Z'-score evaluations of NO measurements

Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (135 nmol/mol), 2 (70 nmol/mol), 3 (35 mol/mol), 4 (15 nmol/mol), 5 (65 nmol/mol), 6 (25 nmol/mol), 7 (490 nmol/mol), 8 (380 nmol/mol), 9 (300 nmol/mol), 10 (200 nmol/mol).

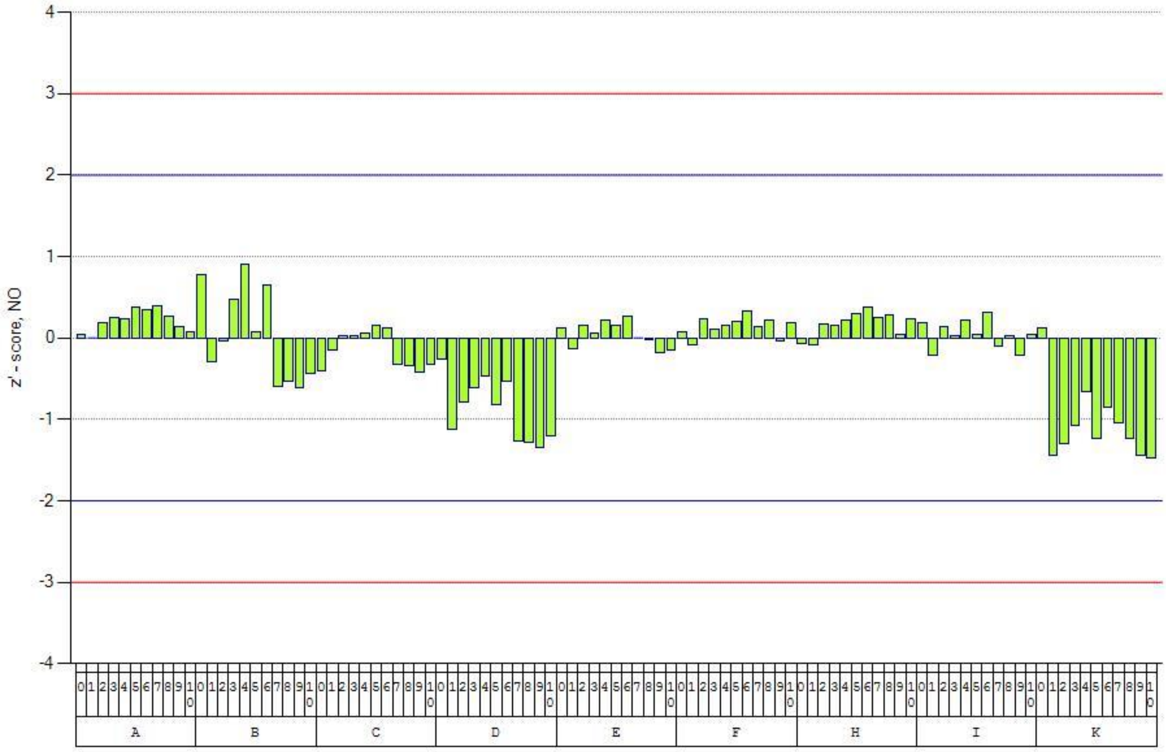
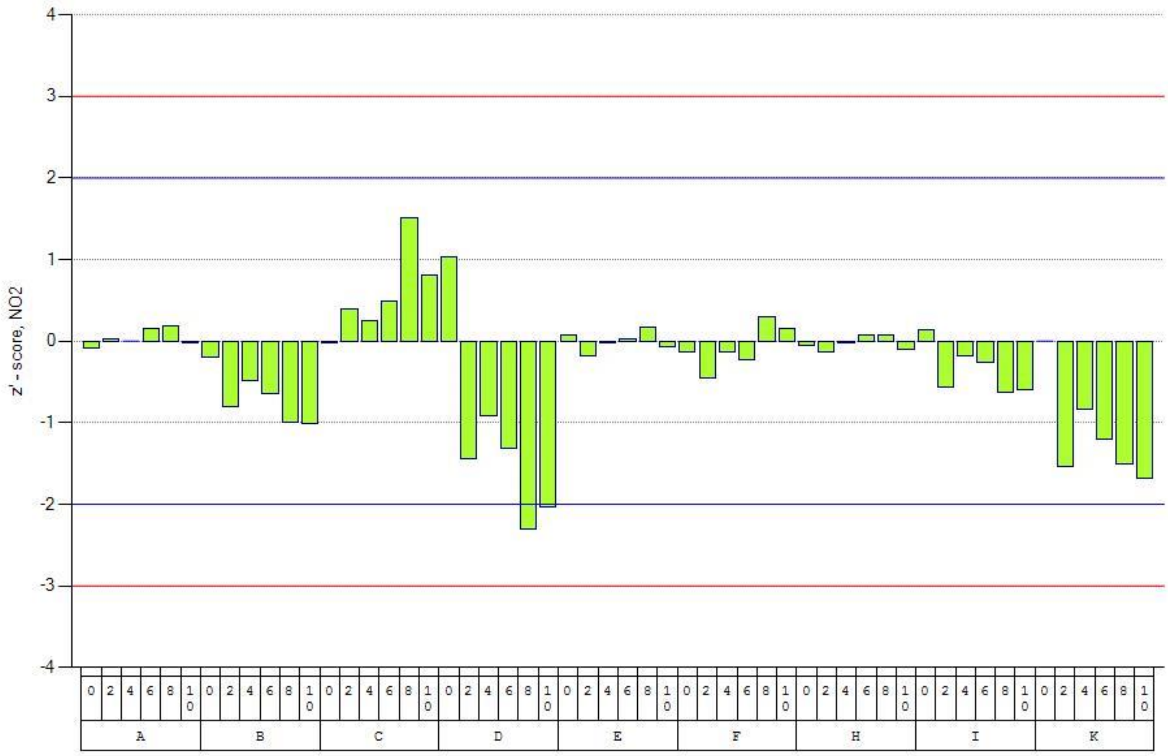


Figure 5: Z'-score evaluations of NO_2 measurements

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (65 nmol/mol), 2 (20 nmol/mol), 3 (40 nmol/mol), 4 (110 nmol/mol), 5 (100 nmol/mol).



5.2 E_n-score

The normalised deviations [13] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}}$$ **Equation 2**

where ***X*** is the assigned/reference value with an expanded uncertainty $\boldsymbol{U_X}$ and $\boldsymbol{x_i}$ is the participant's average value with an expanded uncertainty $\boldsymbol{U_{Xi}}$. Satisfactory results are the ones for which $|E_n| < 1$.

In Figure 6 to Figure 10 the bias of each participant (x_i-X) is plotted and error bars are used to show the value of denominator of equation 2 $\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-score evaluations where, considering the E_n criterion ($|E_n| < 1$), all results with error bars crossing the x-axis are satisfactory. Reported standard uncertainties (0) that are larger than the "standard deviation for proficiency assessments" (σ_p, Table 4) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure. The E_n evaluation showed few unsatisfactory results for different parameters and concentrations, as reported in table 5.

Table 5: Unsatisfactory results according to En-score.

Parameter	Lab Code	Value	Run	En	En evaluation
CO	A	0,736	CO _5	-1,3	unsatisfactory
CO	A	1,831	CO _4	-1,5	unsatisfactory
SO_2	A	36,11	SO_2 _3	-1,2	unsatisfactory
SO_2	A	117,55	SO_2 _1	-1,8	unsatisfactory
SO_2	A	61,52	SO_2 _2	-1,5	unsatisfactory
CO	D	1,9	CO _4	-1,1	unsatisfactory
CO	D	0,8	CO _5	-2,1	unsatisfactory
O_3	D	97,3	O_3 _5	2,2	unsatisfactory
O_3	D	123,38	O_3 _4	2	unsatisfactory
O_3	D	35,38	O_3 _3	1,3	unsatisfactory
CO	E	0,798	CO _5	-1,5	unsatisfactory

Figure 6: Bias of participant's SO_2 measurement results.
Expanded uncertainty of bias for each run is presented as error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p. Laboratory K didn't reported results for this pollutant.

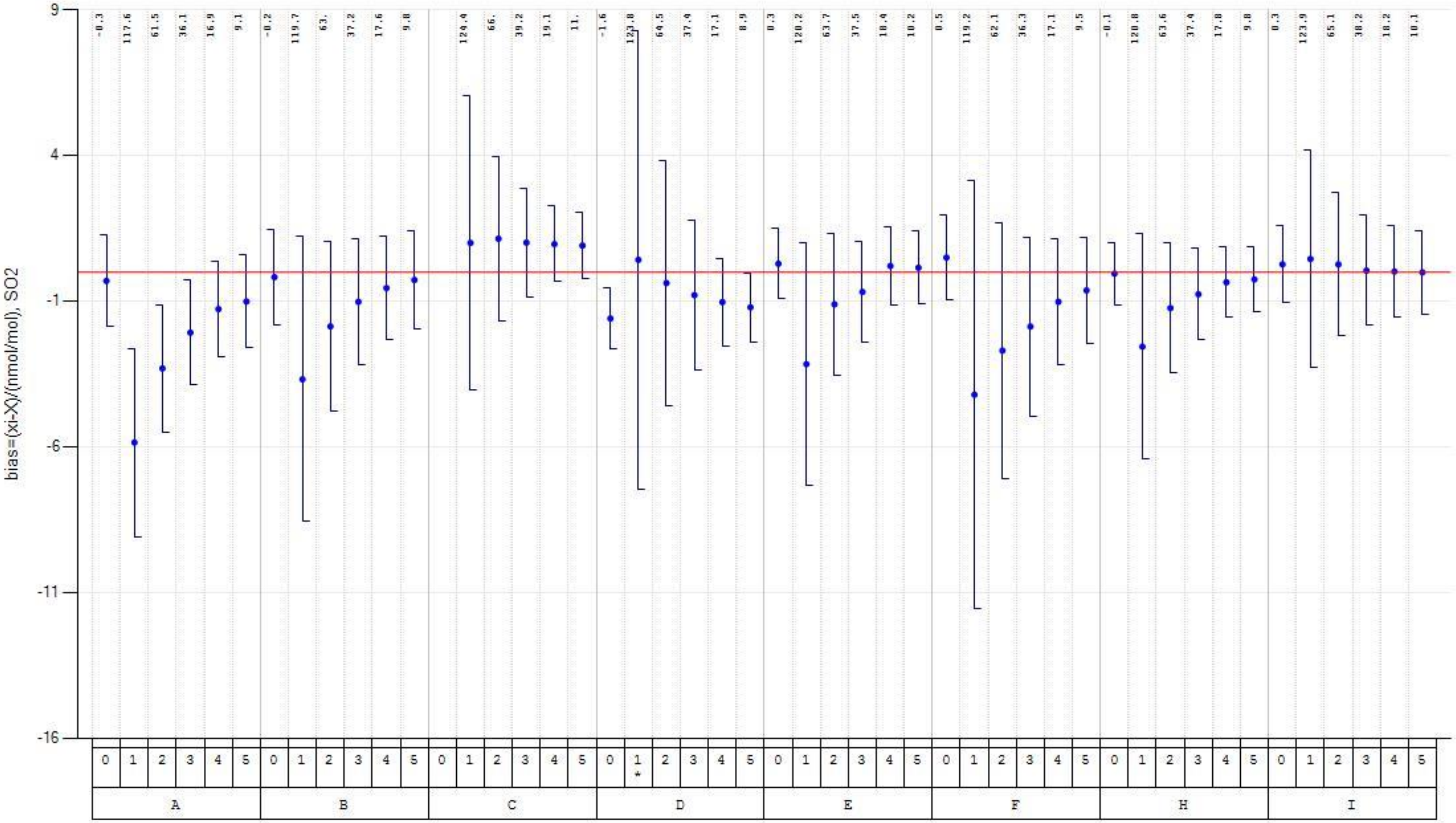


Figure 7: Bias of participant's CO measurement results

Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (µmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p. Laboratory K didn't reported results for this pollutant.

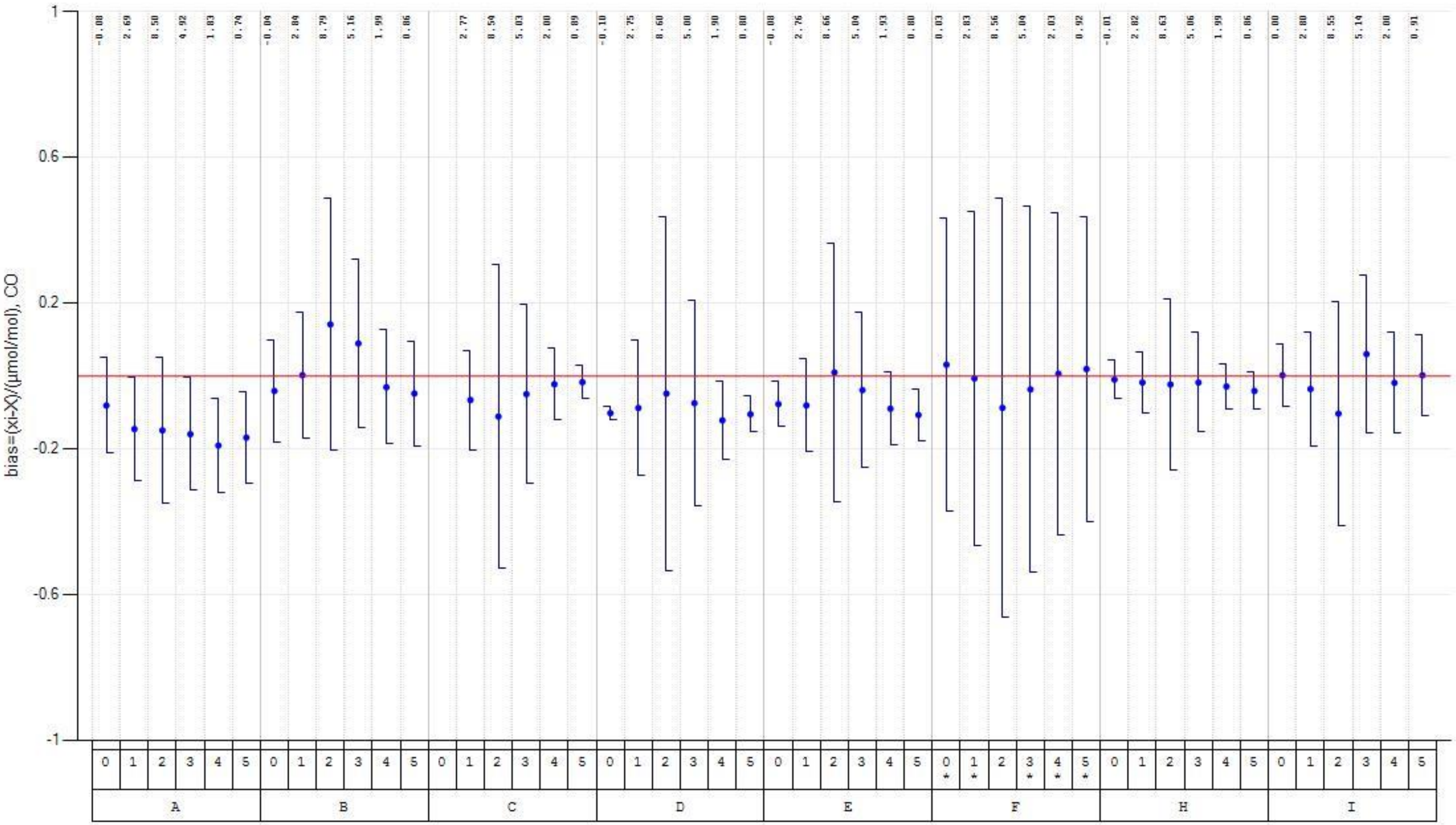


Figure 8: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory.
For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given.
The '*' mark indicates reported standard uncertainties bigger than σ_p.

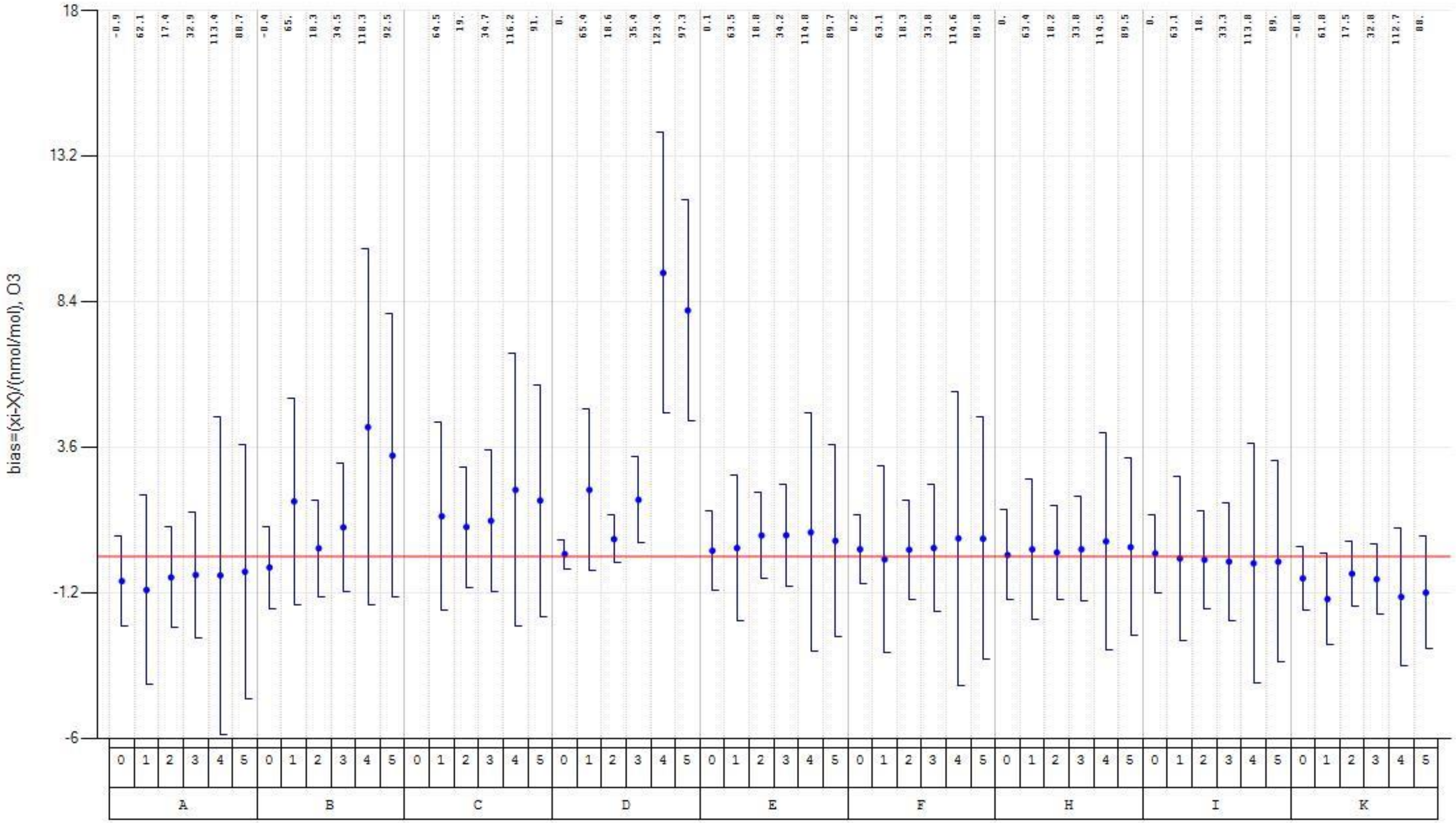


Figure 9: Bias of participant's NO measurement results

Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

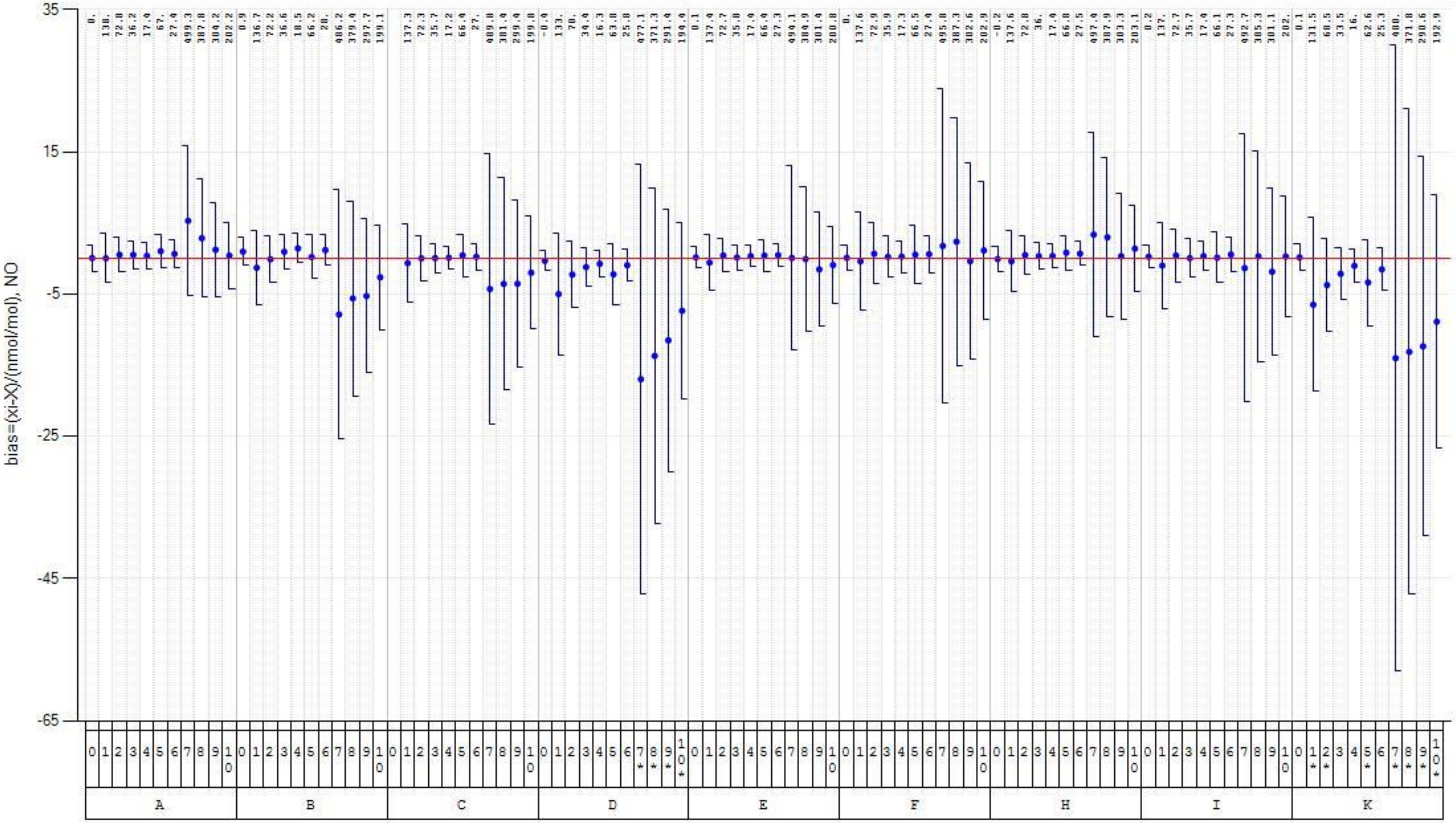
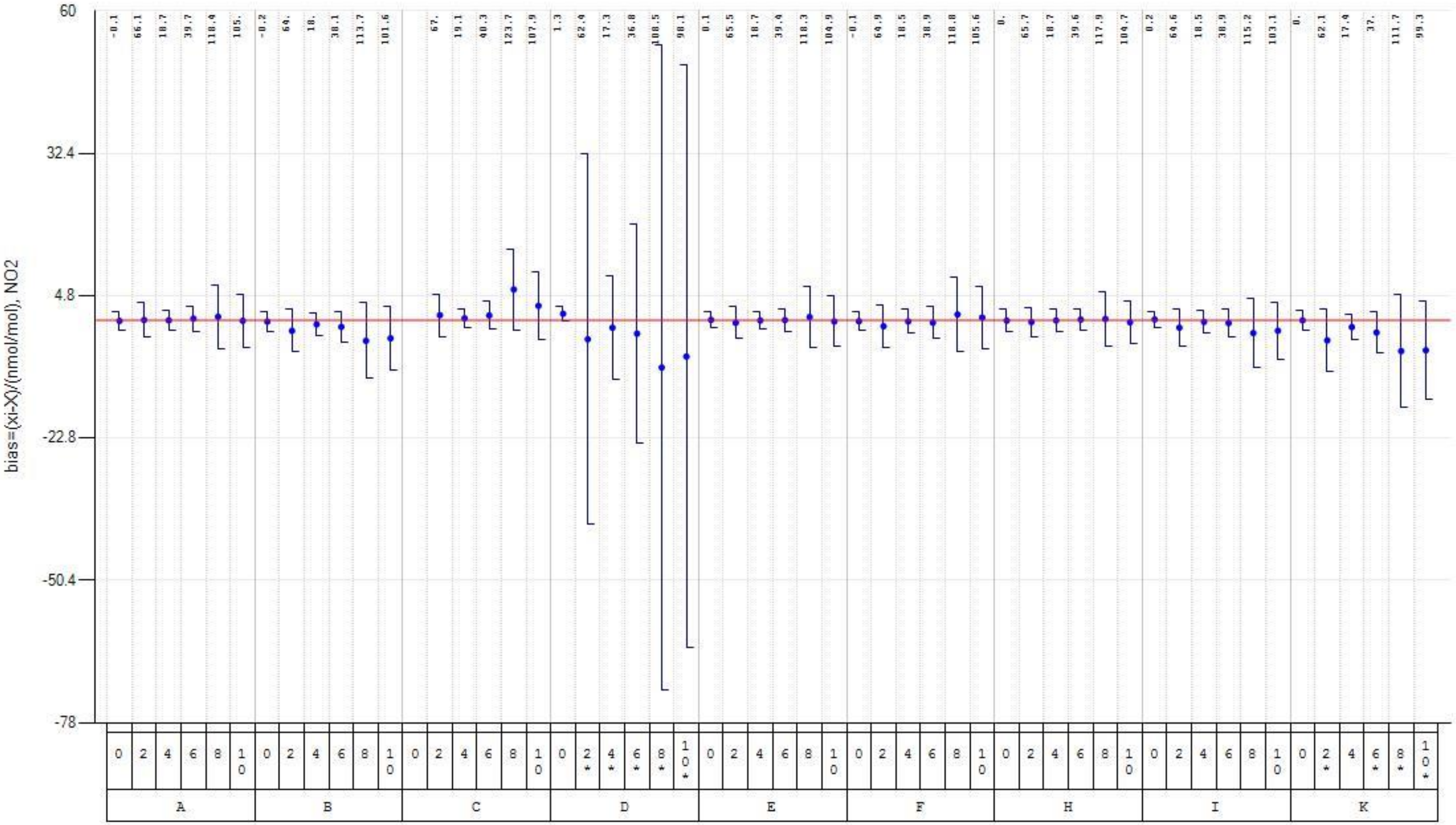


Figure 10: Bias of participant's NO_2 measurement results

Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

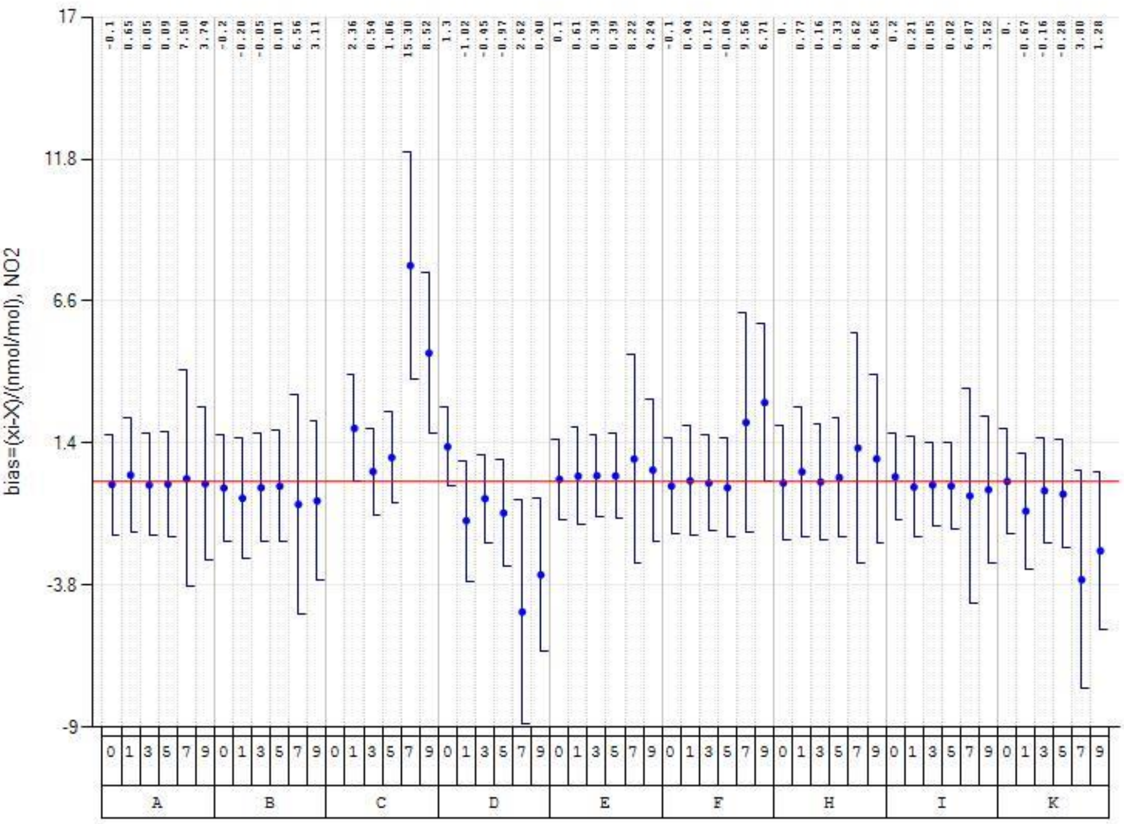
The '*' mark indicates reported standard uncertainties bigger than σ_p.



6. Performance characteristics of individual laboratories

Individual participants' biases were evaluated and are presented in chapter 5 (Figure 6 - 10). Since the results of NO_2 runs 1, 3, 5, 7 and 9 were not treated in proficiency evaluation the bias of these runs are presented in Figure 11.

Figure 11: Bias of participant's NO_2 measurements with error bars representing expanded uncertainty for run numbers 1, 3, 5, 7 and 9.
Within these test gas mixtures there is no gas phase titration to produce NO_2 (see table 3). For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.



6.1 Converter efficiencies of NO_2-to-NO for NOX analysers

Since NO and NO_2 test gases were produced by gas phase titration, it is possible to evaluate the efficiency of the NO_2-to-NO converter of each participant's NO_X analyser. The evaluation takes each participant's NO and NO_2 measurements before and after oxidation by O_3. However, possible minor instabilities in the preparation of the test gas mixtures were not taken into account. The converter efficiency (α) is calculated using Equation 3 [4]:

$$\alpha = \frac{[NO2]_i - [NO2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \qquad \textbf{Equation 3}$$

Ideal value for α is 100%. The evaluation of equation 3 for each participant at different concentration levels are given in Table 6.

Table 6: Efficiency of NO_2-to-NO converters.

Lab code	NO_2 nmol/mol	α (%)
A	65	100,4
	20	99,8
	40	100,1
	110	99,4
	100	99,3
B	65	99,5
	20	99,6
	40	99,7
	110	100,3
	100	100,0
C	65	99,4
	20	100,3
	40	99,6
	110	100,0
	100	99,8
D	65	100,7
	20	98,1
	40	99,6
	110	100,1
	100	100,7
E	65	100,4
	20	99,6
	40	99,8
	110	100,8
	100	100,1

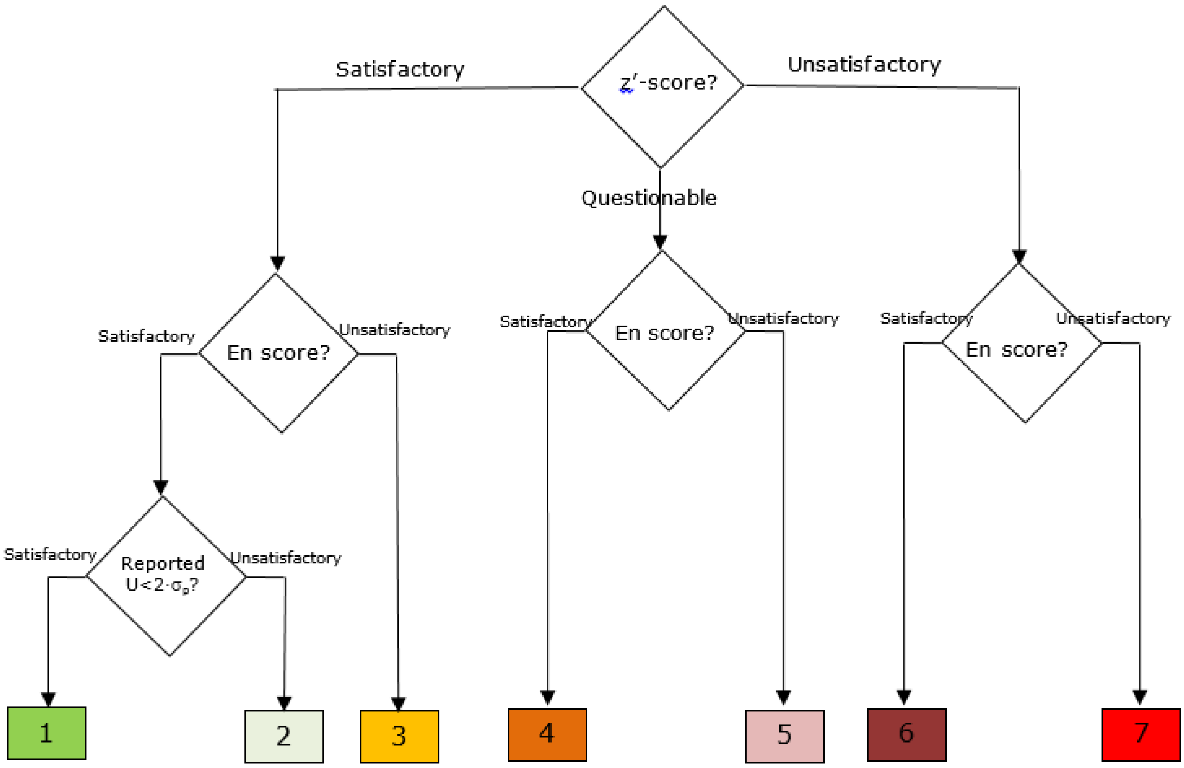
Lab code	NO_2 nmol/mol	α (%)
F	65	99,7
	20	99,2
	40	99,5
	110	100,7
	100	99,3
G	65	99,8
	20	99,9
	40	100,0
	110	101,1
	100	100,1
H	65	100,2
	20	100,0
	40	99,7
	110	99,9
	100	99,9
I	65	100,2
	20	100,5
	40	100,2
	110	100,9
	100	100,5
K	65	99,8
	20	100,7
	40	99,9
	110	99,7
	100	100,3

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) that results in seven categories (1 to 7). The general comments for each category are:

- **1**: measurement result is completely satisfactory
- **2**: measurement result is satisfactory (z'-score satisfactory and En-score satisfactory, but the reported uncertainty is too high
- **3**: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-score unsatisfactory)
- **4**: measurement result is questionable (z'-score questionable), but due to a high reported uncertainty can be considered valid (En-score satisfactory)
- **5**: measurement result is questionable (z'-score questionable and En-score unsatisfactory)
- **6**: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-score satisfactory)
- **7**: measurement result is unsatisfactory (z'-score unsatisfactory and En-score unsatisfactory)

Figure 12: Decision diagram for general assessment of proficiency results.



The results of the ILC were assigned to categories according to the diagram given in Figure 12 and are presented in the following Table 7.

Table 7: General assessment of proficiency results.

"n.r." is referring to values not reported. "U n.r." is referring to Uncertainty values not reported.

	run numb	Ref. conc. level	A	B	C	D	E	F	H	I	K
CO (µmol/mol)	0	0,002	1	1	U n.r.	3	3	2	1	1	n.r.
	1	2,838	1	1	1	1	1	2	1	1	n.r.
	2	8,648	1	1	1	1	1	1	1	1	n.r.
	3	5,075	1	1	1	1	1	2	1	1	n.r.
	4	2,022	3	1	1	3	1	2	1	1	n.r.
	5	0,905	3	1	1	3	3	2	1	1	n.r.
NO (nmol/mol)	0	-0,07	1	1	U n.r.	1	1	1	1	1	1
	1	137,96	1	1	1	1	1	1	1	1	2
	2	72,26	1	1	1	1	1	1	1	1	2
	3	35,65	1	1	1	1	1	1	1	1	1
	4	17,07	1	1	1	1	1	1	1	1	1
	5	65,99	1	1	1	1	1	1	1	1	2
	6	26,78	1	1	1	1	1	1	1	1	1
	7	494,05	1	1	1	2	1	1	1	1	2
	8	384,97	1	1	1	2	1	1	1	1	2
	9	302,94	1	1	1	2	1	1	1	1	2
	10	201,76	1	1	1	2	1	1	1	1	2
NO_2 (nmol/mol)	0	0,03	1	1	U n.r.	1	1	1	1	1	1
	2	66,01	1	1	1	2	1	1	1	1	2
	4	18,74	1	1	1	2	1	1	1	1	1
	6	39,40	1	1	1	2	1	1	1	1	2
	8	117,68	1	1	1	4	1	1	1	1	2
	10	105,11	1	1	1	4	1	1	1	1	2
O_3 (nmol/mol)	0	-0,08	1	1	U n.r.	1	1	1	1	1	1
	1	63,18	1	1	1	1	1	1	1	1	1
	2	18,06	1	1	1	1	1	1	1	1	1
	3	33,51	1	1	1	3	1	1	1	1	1
	4	114,02	1	1	1	5	1	1	1	1	1
	5	89,18	1	1	1	5	1	1	1	1	1
SO_2 (nmol/mol)	0	-0,01	1	1	U n.r.	3	1	1	1	1	n.r.
	1	123,40	3	1	1	2	1	1	1	1	n.r.
	2	64,82	3	1	1	1	1	1	1	1	n.r.
	3	38,19	3	1	1	1	1	1	1	1	n.r.
	4	18,15	1	1	1	1	1	1	1	1	n.r.
	5	10,09	1	1	1	1	1	1	1	1	n.r.

8. Assigned values

The assigned values of tested concentration levels (run) were derived from ERLAP's measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [13].

To foster its reference function ERLAP is participating regularly to key comparisons of the Gas Analysis Working Group within the framework of BIPM's CCQM.

During this ILC ERLAP's SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [6]. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [8]. All flows were measured with a certified molbloc/molbox1 system. For O_3 measurements, the analysers were calibrated using the JRC SRP42 primary standard (constructed by NIST) which has been compared to BIPM primary standard [26]. The photometer absorption cross section uncertainty (1.06%) was included in the uncertainty budget [27], [28].

The reference gas mixture and the calibration experiment evaluation were carried out using two computer applications, the "GUM WORKBENCH" [29] and "B-least" [30] respectively. For extending calibration from the NO to NO_2 channel of NO_X analyser the GPT test was performed to establish the efficiency of NO_2-converter.

ERLAP's measurement results were verified by comparison to the group statistics ($x*$ and $s*$) for every parameter and concentration level of the ILC. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [13]. The verification is taking into account ERLAP's measurement result (X) and its standard uncertainty (u_X) as given in Equation 4 [13]:

$$\frac{|x^* - X|}{\sqrt{\frac{(1.25\, s^*)^2}{p} + u_X^2}} \leq 2 \qquad \text{Equation 4}$$

Where $\boldsymbol{x*}$ and $\boldsymbol{s*}$ represent robust average and robust standard deviation respectively and $\boldsymbol{p}$ is the number of participants. In **table 8** all inputs for Equation 4 are given and all ERLAP's measurement results are confirmed to be valid.

As a group evaluation robust average ($x*$) and robust standard deviation ($s*$) were calculated (applying the procedure described in Annex C of ISO 13528) for each run, and are presented in the following tables.

Table 8: Verification of assigned values (X)

run	unit	X	uX	x*	s*	p
CO _0	µmol/mol	0,00	0,02	-0,04	0,06	9
CO _1	µmol/mol	2,84	0,03	2,79	0,05	9
CO _2	µmol/mol	8,65	0,07	8,60	0,08	9
CO _3	µmol/mol	5,07	0,04	5,05	0,06	9
CO _4	µmol/mol	2,02	0,02	1,98	0,05	9
CO _5	µmol/mol	0,91	0,02	0,86	0,06	9
NO _0	nmol/mol	-0,07	1,42	-0,02	0,19	10
NO _1	nmol/mol	137,96	2,43	137,18	0,73	10
NO _2	nmol/mol	72,26	1,76	72,42	0,46	10
NO _3	nmol/mol	35,65	1,51	35,77	0,33	10
NO _4	nmol/mol	17,07	1,44	17,30	0,22	10
NO _5	nmol/mol	65,99	1,72	66,27	0,47	10
NO _6	nmol/mol	26,78	1,48	27,20	0,38	10
NO _7	nmol/mol	494,05	7,14	491,90	5,95	10
NO _8	nmol/mol	384,97	5,65	383,57	4,39	10
NO _9	nmol/mol	302,94	4,52	300,63	3,09	10
NO _10	nmol/mol	201,76	3,21	200,73	2,27	10
NO2 _0	nmol/mol	0,03	1,43	0,02	0,16	10
NO2 _1	nmol/mol	0,42	1,73	0,36	0,50	10
NO2 _2	nmol/mol	66,01	2,01	65,04	1,40	10
NO2 _3	nmol/mol	0,18	1,46	0,09	0,20	10
NO2 _4	nmol/mol	18,74	1,48	18,57	0,26	10
NO2 _5	nmol/mol	0,19	1,52	0,08	0,32	10
NO2 _6	nmol/mol	39,40	1,63	39,05	0,84	10
NO2 _7	nmol/mol	7,40	3,77	7,48	1,82	10
NO2 _8	nmol/mol	117,68	4,20	116,90	2,95	10
NO2 _9	nmol/mol	3,82	2,57	3,82	1,37	10
NO2 _10	nmol/mol	105,11	3,05	104,16	2,07	10
O3 _0	nmol/mol	-0,08	0,48	-0,06	0,26	10
O3 _1	nmol/mol	63,18	1,10	63,44	1,21	10
O3 _2	nmol/mol	18,06	0,49	18,22	0,57	10
O3 _3	nmol/mol	33,51	0,65	33,85	0,86	10
O3 _4	nmol/mol	114,02	1,95	114,76	1,58	10
O3 _5	nmol/mol	89,18	1,53	89,74	1,28	10
SO2 _0	nmol/mol	-0,01	1,03	0,05	0,46	9
SO2 _1	nmol/mol	123,40	2,34	121,45	2,81	9
SO2 _2	nmol/mol	64,82	1,53	63,81	1,63	9
SO2 _3	nmol/mol	38,19	1,22	37,49	1,06	9
SO2 _4	nmol/mol	18,15	1,09	17,80	0,77	9
SO2 _5	nmol/mol	10,09	1,05	9,81	0,62	9

By comparison to the robust averages (x*) with taking into account the standard uncertainties of assigned values (uX), and robust standard deviations (s*) as denoted by Equation 4.

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. The relative differences between beginning and end measurements are calculated.

$$u_X^2 = u_{X'}^2 + \left(X \cdot u_{\mathrm{hom}\,ogeneity}\right)^2$$ **Equation 5**

The upper and lower limits of bias due to homogeneity were evaluated to be smaller than 0.5% which constitutes the relative standard uncertainty of 0.3% of each concentration level assuming a rectangular distribution of the bias. The standard uncertainties of assigned/reference values (u_X) were calculated with Equation 5 and used in the proficiency evaluations of chapter 3.

All calculations about the homogeneity testing data are retained by ERLAP, they are not published in this ILC report but, are available on request.

9. Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties.

In terms of the criteria imposed by the European Directive (σ_p) 86% of the results reported during this ILC (see Table 7) by AQUILA laboratories fall into category '1' and are satisfactory both in terms of measured values and evaluated uncertainties.

Among the remaining all results presented satisfactory measured values, but the evaluated uncertainties were either too high, category '2' (8%), or too small, category '3' (4%). Four values were found questionable for z'-score but two of them were satisfactory (category 4, 1% of total values) and two were unsatisfactory for En-score (category 5, 1% of total values). No values were found unsatisfactory for both value and uncertainty (category 6 and 7).

Table 9: Flags summary

ILC	Site	Categories %						
		1	2	3	4	5	6	7
Apr-08	Ispra (IT)	68.4	18.1	7.3	1.0	1.0	2.6	1.6
Oct-08 (I)	Ispra (IT)	37.9	40.8	14.2	0.6	3.6	1.0	1.9
Oct-08 (II)	Ispra (IT)	34.3	38.9	23.7	1.0	2.0	0.0	0.0
Sep-09	Langen (DE)	60.8	29.9	3.1	4.1	1.0	1.0	0.0
Oct-09	Ispra (IT)	85.0	5.7	7.5	0.4	1.4	0.0	0.0
Jun-10	Ispra (IT)	84.6	8.1	4.4	0.7	2.3	0.0	0.0
Sep-11	Ispra (IT)	86.1	7.9	5.4	0.0	0.3	0.0	0.3
Oct-11 (I)	Ispra (IT)	78.6	12.5	7.6	0.0	1.3	0.0	0.0
Oct-11 (II)	Langen (DE)	59.4	39.9	0.0	0.7	0.0	0.0	0.0
Jun-12	Ispra (IT)	92.2	0.5	7.3	0.0	0.0	0.0	0.0
Sep-13	Langen (DE)	75.7	20.9	2.0	0.0	1.4	0.0	0.0
Sep-13	Ispra (IT)	89.4	7.3	3.3	0.0	0.0	0.0	0.0
Oct-13	Ispra (IT)	86.8	8.9	3.6	0.4	0.4	0.0	0.0
May-14	Ispra (IT)	81.8	15.2	1.1	0.0	0.7	0.0	1.1
Oct-15	Langen (DE)	73.2	23.9	0.7	1.4	0.0	0.7	0.0
Oct-15 (I)	Ispra (IT)	90.2	7.6	1.6	0.3	0.3	0.0	0.0
Oct-15 (II)	Ispra (IT)	75.6	10.8	7.3	0.6	3.5	0.0	2.2
Jun-16	Ispra (IT)	79.3	17.8	2.9	0.0	0.0	0.0	0.0
Jun-17 (I)	Ispra (IT)	92.8	4.3	1.8	0.0	0.7	0.0	0.4
Jun-17 (II)	Ispra (IT)	78.1	11.5	6.5	0.0	1.9	0.0	1.9
Jun-18	Ispra (IT)	95.6	1.3	3.1	0.0	0.0	0.0	0.0
Sep-18	Langen (DE)	59.6	40.4	0.0	0.0	0.0	0.0	0.0
May-19	Ispra (IT)	86.0	8.0	4.0	1.0	1.0	0.0	0.0

As in previous ILC, the adopted criteria for high concentrations were the standard deviations for proficiency assessment, deriving from the European Standards' uncertainty requirements.

The reproducibility standard deviation obtained at this (0) and previous ILC [20], [21], [22], [23], [24], [25], [33], [34], [35], [36], [37], [38], [39], [40], [41], [43], [44], [45], [46], [47] and [48] is comparable to the mentioned criteria. On the other hand, the uncertainty criteria for zero levels were those set in AQUILA's position paper [12].

In this exercise 99% of the results in the z'-score evaluations were satisfactory and only 1% questionable.

Table 10: Z'-score summary

ILC	*Site*	*Satisfactory (%)*	*Questionable (%)*	*Unsatisfactory (%)*
June/05	Ispra (IT)	94.7	2.3	3.0
June/07	Ispra (IT)	97.8	1.9	0.3
October/07	Essen (DE)	93.2	4.6	2.2
April/08	Ispra (IT)	93.8	2.1	4.1
October/08_1	Ispra (IT)	92.9	4.2	2.9
October/08_2	Ispra (IT)	97.0	3.0	0.0
September/09	Langen (DE)	94.3	4.7	0.9
October/09	Ispra (IT)	98.2	1.8	0.0
June/10	Ispra (IT)	97.0	3.0	0.0
September/11	Ispra (IT)	99.4	0.3	0.3
October/11	Ispra (IT)	98.7	1.3	0.0
October/11	Langen (DE)	99.3	0.7	0.0
June/12	Ispra (IT)	100.0	0.0	0.0
September/13	Langen (DE)	98.6	1.4	0.0
September/13	Ispra (IT)	100.0	0.0	0.0
October/13	Ispra (IT)	99.3	0.7	0.0
May/14	Ispra (IT)	98.1	0.7	1.1
October/15	Langen (DE)	97.9	1.4	0.7
October/15_1	Ispra (IT)	99.4	0.6	0.0
October/15_2	Ispra (IT)	93.7	4.1	2.2
June/16	Ispra (IT)	100	0.0	0.0
June/17_1	Ispra (IT)	98.9	0.7	0.4
June/17_2	Ispra (IT)	96.2	1.9	1.9
June/18	Ispra (IT)	100	0.0	0.0
Sep/18	Langen (DE)	100	0.0	0.0
May/19	Ispra (IT)	99.0	1.0	0.0

Comparability of results among AQUILA participants at the highest concentration level is acceptable for all pollutant measurements.

The relative reproducibility limits, at the highest studied concentration levels, are 6.7% for SO_2, 3.3% for CO, 8.7% for O_3, for NO 4.8% and for NO_2 11.8% all within the objective derived from criteria imposed by the European Commission (σ_p see Table 4).

During this ILC the performance of all NRL was generally satisfactory. No values were identified as outliers.

10. References

[1] EC *Directive 2008/50/EC of the European Parliament and of the Council* of 21 May 2008 on ambient air quality and cleaner air for Europe, L 152, 11.06.2008

[2] CEN, EN 14626:2012, *ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infrared spectroscopy*

[3] CEN, EN 14212:2012, *ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence*

[4] CEN, EN 14211:2012, *ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence*

[5] CEN, EN 14625:2012, *ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry*

[6] ISO 6143:2001, *Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures*

[7] ISO 6144:2003, *Gas analysis - Preparation of calibration gas mixtures - Static volumetric method*

[8] ISO 6145-7:2001, *Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 7: Thermal mass-flow controllers*

[9] Mücke H.-G., *Air quality management in the WHO European Region – Results of a quality assurance and control programme on air quality monitoring (1994-2004)*, Environment International, EI-01718. 2008

[10] Mücke H.-G. et al., *European Intercomparison workshop on air quality monitoring vol.4 – Measuring NO, NO_2, O_3 and SO_2 – Air Hygiene Report 13*, WHO Collaboration Centre for Air Quality Management and Air Pollution Control, ISSN 0938 – 9822. 2000

[11] AQUILA Network of the National Reference Laboratories of the Member States [online]: Available: https://ec.europa.eu/jrc/en/aquila.

[12] AQUILA POSITION PAPER N. 37, *Protocol for intercomparison exercise. Organisation of intercomparison exercises for gaseous air pollution for EU national air quality reference laboratories and laboratories of the WHO EURO region*, 2008 Available: https://ec.europa.eu/jrc/sites/jrcsh/files/aquila-n_37-intercomparison-exercise protocol 2008.pdf

[13] ISO 13528:2015, *Statistical methods for use in proficiency testing by inter-laboratory comparisons*

[14] ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions*

[15] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[16] ISO 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values*

[17] De Saeger E. et al., *Harmonisation of Directive 92/72/EEC on air pollution by ozone*, EUR 17662, 1997

[18] De Saeger E. et al., *European comparison of Nitrogen Dioxide calibration methods*, EUR 17661, 1997

[19] ISO 15337:2009, *Ambient air - Gas phase titration - Calibration of analysers for ozone*

[20] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO_2, CO, O_3, NO and NO_2 carried out in June 2007 in Ispra*. JRC scientific and technical reports. EUR 23804. 2009

[21] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO_2, CO, O_3, NO and NO_2 - April 2008.* JRC scientific and technical reports. EUR 23805. 2009

[22] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO_2, CO, O_3, NO and NO_2 6-9 October 2008.* JRC scientific and technical reports. EUR 23806. 2009

[23] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO_2, CO, O_3, NO and NO_2 13-16 October 2008.* JRC scientific and technical reports. EUR 23807. 2009

[24] Belis C. A. et al. *The evaluation of the Interlaboratory comparison Exercise for SO_2, CO, O_3, NO and NO_2 Langen 20-25 September 2009.* EUR 24376. 2010

[25] Belis C. A. et al. *The evaluation of the Interlaboratory comparison Exercise for SO_2, CO, O_3, NO and NO_2 19-22 October 2009.* EUR 24476. 2010

[26] Viallon J. et al. *Final report, on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with JRC, 2008.* Metrologia 46 08017, 2009. doi: 10.1088/0026-1394/46/1A/08017

[27] Viallon, J., et al. *International comparison CCQM-P28: Ozone at ambient level*, Metrologia 43, Tech. Suppl., 08010, 2006. doi:10.1088/0026-1394/43/1A/08010

[28] Tanimoto, H., et al. *Intercomparison of ultraviolet photometry and gas-phase titration techniques for ozone reference standards at ambient levels*, Journal of Geophysical Research, vol. 111, D16313, 2006. doi:10.1029/2005JD006983

[29] ISO, *Guide to the expression of uncertainty in measurements,* Geneva, 1995, ISBN 92-67-10188-9

[30] VDI 2449 Part3: 2001, *Measurement methods test criteria- General method for the determination of the uncertainty of calibratable measurement methods.*

[31] Mücke H-G, et al. *European Intercomparison Workshops on Air Quality Monitoring. Vol. 2 – Measuring of CO, NO, NO_2 and O_3 – Air Hygiene Report 9.* Berlin, Germany: WHO Collaborating Centre for Air Quality Management and Air Pollution Control; 1996. ISSN 0938-9822.

[32] ISO 17043:2010, *Conformity assessment - General requirements for proficiency testing*

[33] Barbiere M. et al. *The evaluation of the Interlaboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 Ispra 14-17 June 2010.* EUR 24943. 2011

[34] Barbiere M. et al. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2, 11th-14th June 2012 Ispra.* EUR 25536. 2012

[35] Barbiere M. et al. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2, Langen 23rd-28th October 2011.* EUR 25387. 2012

[36] Barbiere M. et al. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2, 03rd-06th October 2011 Ispra.* EUR 25386. 2012

[37] Barbiere M. et al. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2, 26th-29th September 2011 Ispra.* EUR 25385. 2012

[38] Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. *Evaluation of the Laboratory Comparison Exercise for NO, NO_2, SO_2, CO, and O_3 Langen (D) 1st-6th September 2013.* EUR 26578. 2014

[39] Barbiere M., Lagler F., *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 30st September-3rd October 2013 Ispra.* EUR 26604. 2014

[40] Barbiere M., Lagler F., *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 7^{st}-10^{th} October 2013 Ispra.* EUR 26639. 2014

[41] Barbiere M., Lagler F., *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 19^{th}-22^{nd} May 2014 Ispra.* EUR 27199. 2014

[42] EC COMMISSION DIRECTIVE (EU) 2015/1480 of 28 August 2015 (L226/4) amending several annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality

[43] Lagler F., Barbiere M., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO2 12th-15th October 2015 Ispra.* EUR 28097. 2016

[44] Barbiere M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 19th-23rd October 2015 Ispra.* EUR 28047. 2016

[45] Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. *Evaluation of the Laboratory Comparison Exercise for NO, NO_2, SO_2, CO, and O_3 Langen (D) 4th-9th October 2015.* EUR 27918. 2016

[46] Barbiere M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 13-16 June 2016, Ispra.* EUR 28610. 2017

[47] Barbiere M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 19-22 June 2017, Ispra.* EUR 29268. 2017

[48] Barbiere M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 26-29 June 2017, Ispra.* EUR 29271. 2017

[49] Barbiere M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 4-7 June 2018, Ispra.* EUR 29671. 2018

[50] Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. *Evaluation of the Laboratory Comparison Exercise for NO, NO_2, SO_2, CO, and O_3 Langen (D) 2-7 September 2018.* EUR 29694. 2018

List of abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
CEN	European Committee for Standardization
CO	Carbon monoxide
CRM	Certified Reference Material
DQO	Data Quality Objective
ERLAP	European Reference Laboratory for Air Pollution
EC	European Commission
GPT	Gas Phase Titration
ILC	Inter-Laboratory Comparison Exercise
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	The oxides of nitrogen, the sum of NO and NO_2
NRL	National Reference Laboratory
O_3	Ozone
SO_2	Sulphur dioxide
VDI	Verein Deutscher Ingenieure
WHO-CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols

α	converter efficiency (EN 14211)
E_n	E_n–score statistic (ISO 13528)
r	repeatability limit (ISO 5725)
R	reproducibility limit (ISO 5725)
σ_p	standard deviation for proficiency assessment (ISO 13528)
x*	robust average (Annex C ISO 13528)
s*	robust standard deviation (Annex C ISO 13528)
s_r	repeatability standard deviation (ISO 5725)
s_R	reproducibility standard deviation (ISO 5725)
U_X	expanded uncertainty of the assigned/reference value (ISO 13528)
U_{xi}	expanded uncertainty of the participant's value (ISO 13528)
u_X	standard uncertainty of the assigned/reference value (ISO 13528)
X	assigned/reference value (ISO 13528)
x_i	average of three values reported by the participant *i* (for particular parameter and concentration level) (ISO 5725)
$x_{i,j}$	j-the reported value of participant i (for particular parameter and concentration level) (ISO 5725)
z'	z'-score statistic (ISO 13528)

List of figures

List of tables

Annex A: The results of the ILC

In this annex are reported participant's results, presented both in tables and graphs. For all mixture concentration generated (run), participants were asked to report 3 results representing 30 minutes measurement each (x_i).

In this annex are presented the reported data and their uncertainty $u(x_i)$ and $U(x_i)$ expressed in mol/mol units.

For all the runs except concentration levels 0, also average (x_i) and standard deviation (s_i) of each participant are presented.

The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties (Ux_i) are indicated with error bars.

Reported values for SO_2

Table 11: Reported values for SO_2 run 0.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	-0.31	-0.18	1.27	-1.60	0.28	0.49	-0.01	-0.06	0.26
u(xi)	0.59	0.64			0.31	0.51	0.52	0.16	0.41
U(xi)	1.17	1.27		-0.01	0.62	1.03	1.03	0.31	0.82

Figure 13: Reported values for SO_2 run 0.

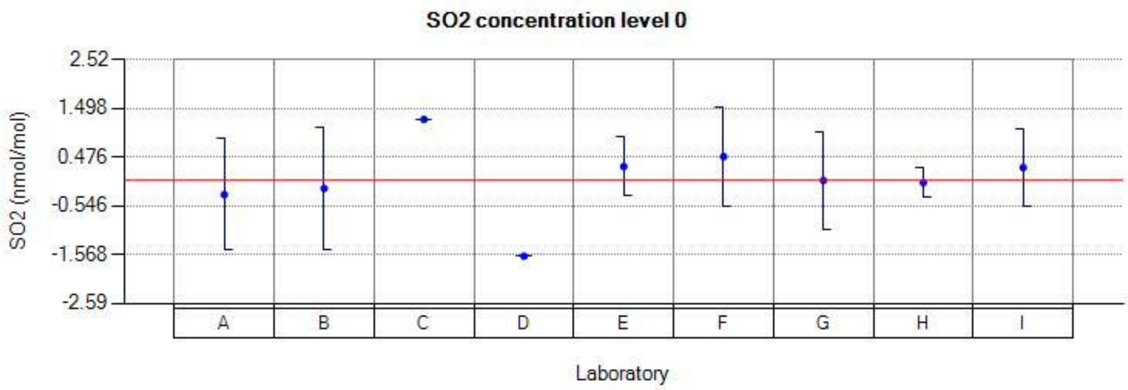


Table 12: Reported values for SO_2 run 1

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	117.39	119.47	124.17	123.55	120.56	118.97	123.28	120.75	123.88
xi, 2	117.65	119.68	124.57	123.90	119.44	119.29	123.50	120.87	123.73
xi, 3	117.60	120.02	124.47	124.00	120.71	119.31	123.41	120.90	123.95
xi	117.54	119.72	124.40	123.81	120.23	119.19	123.39	120.84	123.85
si	0.13	0.27	0.20	0.23	0.69	0.19	0.11	0.07	0.11
u(xi)	1.12	2.15	2.24	3.76	1.73	3.48	1.11	1.53	1.46
U(xi)	2.23	4.29	4.48	7.52	3.46	6.96	2.22	3.07	2.92

Figure 14: Reported values for SO_2 run 1.

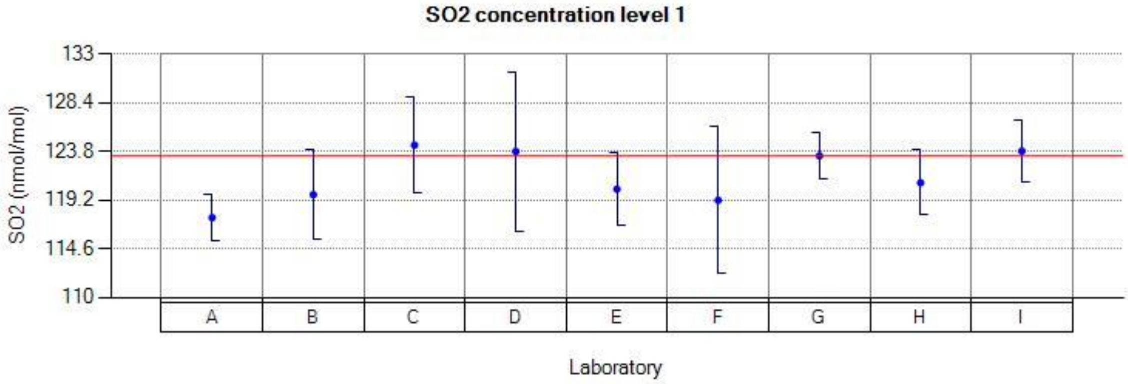


Table 13: Reported values for SO_2 run 2.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	61.60	62.91	66.03	64.40	63.25	62.13	64.81	63.56	65.00
xi, 2	61.48	62.89	65.99	64.45	63.77	62.14	64.83	63.64	65.09
xi, 3	61.49	63.07	65.88	64.50	64.13	62.12	64.83	63.56	65.19
xi	61.52	62.95	65.96	64.45	63.71	62.13	64.82	63.58	65.09
si	0.06	0.09	0.07	0.05	0.44	0.01	0.01	0.04	0.09
u(xi)	0.77	1.25	1.19	1.96	0.95	2.05	0.74	0.82	0.96
U(xi)	1.55	2.50	2.38	3.91	1.90	4.11	1.48	1.63	1.92

Figure 15: Reported values for SO_2 run 2.

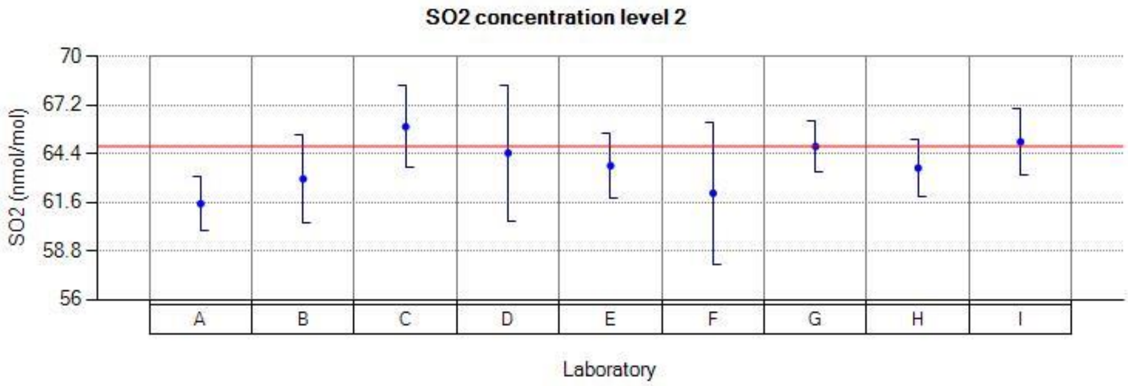


Table 14: Reported values for SO_2 run 3.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	36.06	37.16	39.30	37.30	37.09	36.37	38.15	37.36	38.18
xi, 2	36.17	37.16	39.10	37.45	37.86	36.26	38.17	37.47	38.29
xi, 3	36.09	37.20	39.19	37.45	37.59	36.32	38.24	37.45	38.24
xi	36.10	37.17	39.19	37.40	37.51	36.31	38.18	37.42	38.23
si	0.05	0.02	0.10	0.08	0.39	0.05	0.04	0.05	0.05
u(xi)	0.66	0.90	0.71	1.14	0.61	1.41	0.60	0.49	0.72
U(xi)	1.31	1.80	1.42	2.28	1.23	2.82	1.20	0.99	1.44

Figure 16: Reported values for SO_2 run 3.

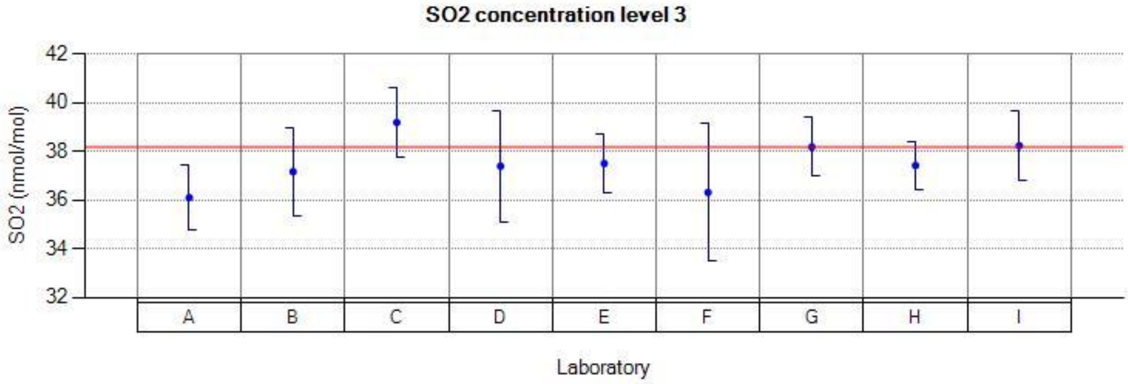


Table 15: Reported values for SO_2 run 4.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	16.84	17.63	19.11	17.10	18.39	16.98	18.13	17.82	18.17
xi, 2	16.93	17.56	19.14	17.15	18.49	17.11	18.15	17.82	18.14
xi, 3	16.87	17.61	19.07	17.10	18.20	17.29	18.16	17.76	18.21
xi	16.88	17.60	19.10	17.11	18.36	17.12	18.14	17.80	18.17
si	0.04	0.03	0.03	0.02	0.14	0.15	0.01	0.03	0.03
u(xi)	0.60	0.70	0.35	0.52	0.40	0.93	0.54	0.25	0.56
U(xi)	1.21	1.41	0.70	1.04	0.81	1.86	1.08	0.50	1.12

Figure 17: Reported values for SO_2 run 4.

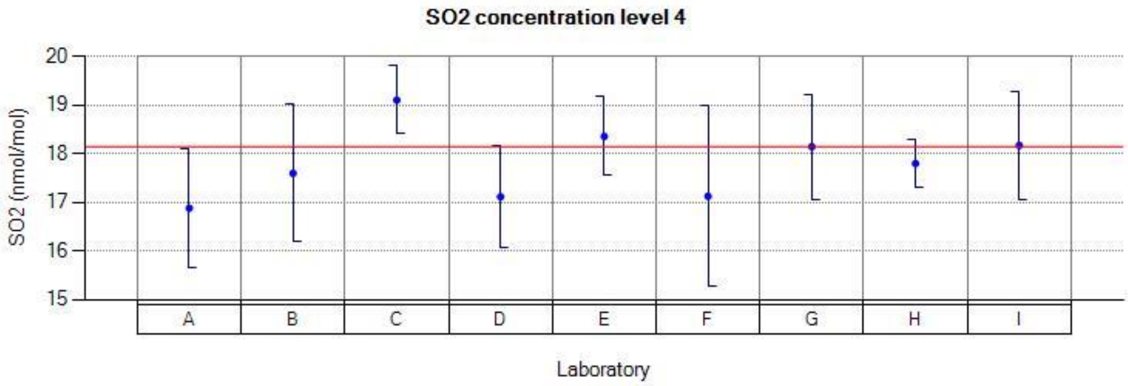
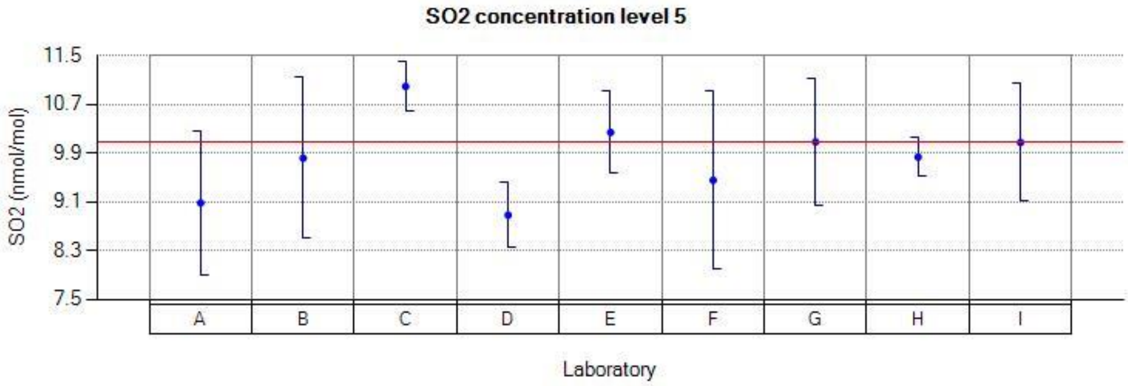


Table 16: Reported values for SO_2 run 5.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	9.18	9.81	11.14	8.90	10.15	9.46	10.09	9.82	10.06
xi, 2	8.99	9.84	10.93	8.85	10.11	9.40	10.10	9.81	10.10
xi, 3	9.08	9.81	10.92	8.90	10.47	9.51	10.07	9.88	10.07
xi	9.08	9.82	10.99	8.88	10.24	9.45	10.08	9.83	10.07
si	0.09	0.01	0.12	0.02	0.19	0.05	0.01	0.03	0.02
u(xi)	0.59	0.66	0.20	0.27	0.34	0.74	0.52	0.16	0.49
U(xi)	1.18	1.32	0.40	0.54	0.68	1.47	1.05	0.32	0.97

Figure 18: Reported values for SO_2 run 5.



Reported values for CO

Table 17: Reported values for CO run 0.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	-0.079	-0.039	-0.096	-0.100	-0.075	0.033	0.002	-0.008	0.004
u(xi)	0.065	0.069		-0.002	0.029	0.200	0.009	0.025	0.043
U(xi)	0.129	0.139		-0.004	0.059	0.401	0.018	0.050	0.085

Figure 19: Reported values for CO run 0.

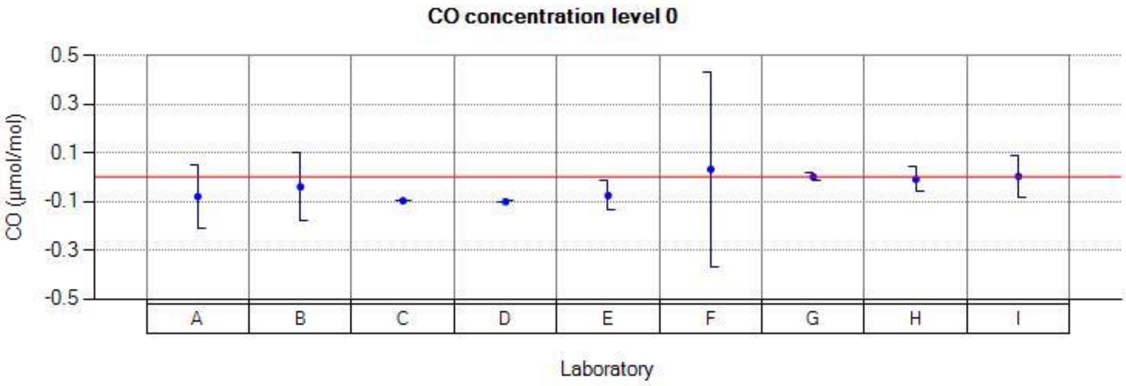


Table 18: Reported values for CO run 1.

values	laboratories								
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi, 1	2.698	2.843	2.760	2.800	2.749	2.830	2.836	2.817	2.792
xi, 2	2.690	2.843	2.774	2.750	2.760	2.831	2.837	2.822	2.809
xi, 3	2.688	2.833	2.781	2.700	2.763	2.832	2.840	2.822	2.805
xi	2.692	2.840	2.772	2.750	2.757	2.831	2.838	2.820	2.802
si	0.005	0.006	0.011	0.050	0.007	0.001	0.002	0.003	0.009
u(xi)	0.070	0.085	0.067	0.092	0.062	0.228	0.011	0.039	0.078
U(xi)	0.139	0.171	0.134	0.183	0.125	0.457	0.021	0.078	0.155

Figure 20: Reported values for CO run 1.

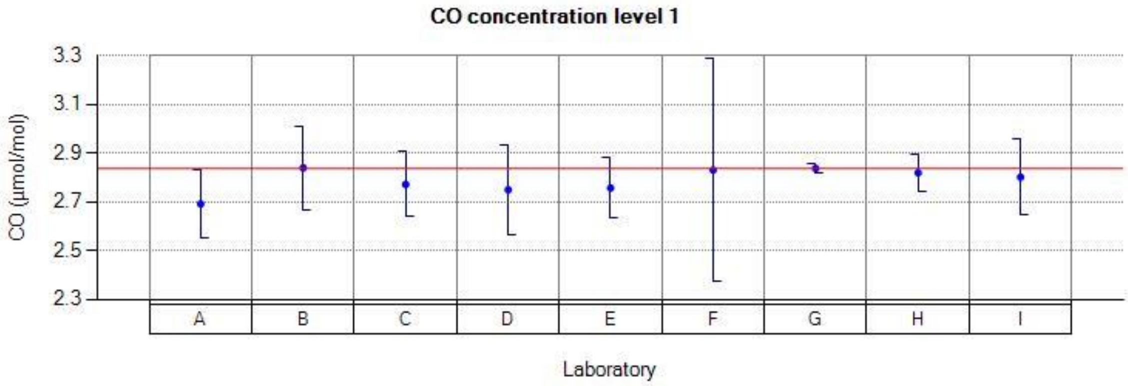


Table 19: Reported values for CO run 2

values	laboratories								
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
xi, 1	8.510	8.790	8.532	8.600	8.661	8.560	8.648	8.624	8.543
xi, 2	8.502	8.790	8.539	8.600	8.657	8.561	8.649	8.629	8.547
xi, 3	8.486	8.790	8.539	8.600	8.657	8.562	8.648	8.623	8.546
xi	8.499	8.790	8.537	8.600	8.658	8.561	8.648	8.625	8.545
si	0.012	0.000	0.004	0.000	0.002	0.001	0.001	0.003	0.002
u(xi)	0.094	0.169	0.205	0.240	0.174	0.286	0.023	0.112	0.151
U(xi)	0.188	0.338	0.410	0.480	0.349	0.571	0.046	0.223	0.301

Figure 21: Reported values for CO run 2.

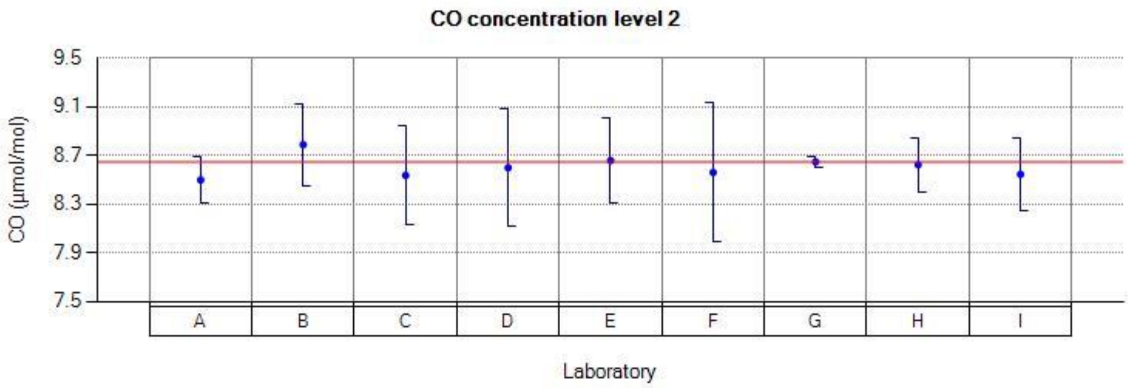


Table 20: Reported values for CO run 3.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	4.916	5.167	5.020	5.000	5.036	5.037	5.074	5.056	5.131
xi, 2	4.914	5.167	5.027	5.000	5.033	5.040	5.075	5.057	5.136
xi, 3	4.915	5.157	5.027	5.000	5.040	5.038	5.075	5.059	5.138
xi	4.915	5.164	5.025	5.000	5.036	5.038	5.075	5.057	5.135
si	0.001	0.006	0.004	0.000	0.004	0.002	0.001	0.002	0.004
u(xi)	0.074	0.114	0.121	0.140	0.104	0.250	0.015	0.065	0.107
U(xi)	0.149	0.228	0.242	0.279	0.208	0.501	0.029	0.130	0.214

Figure 22: Reported values for CO run 3.

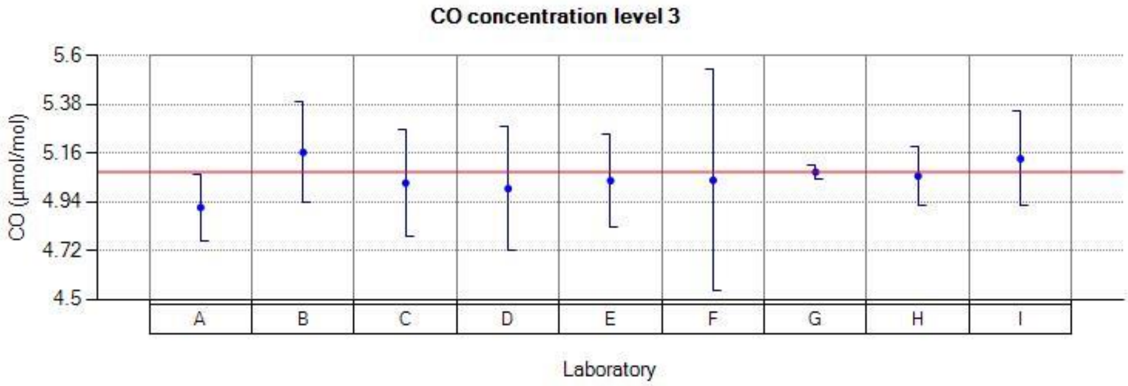


Table 21: Reported values for CO run 4.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	1.838	1.991	1.997	1.900	1.933	2.028	2.022	1.998	2.002
xi, 2	1.828	1.991	2.000	1.900	1.932	2.030	2.021	1.991	2.000
xi, 3	1.827	1.991	2.001	1.900	1.930	2.026	2.022	1.989	2.006
xi	1.831	1.991	1.999	1.900	1.932	2.028	2.022	1.993	2.003
si	0.006	0.000	0.002	0.000	0.002	0.002	0.001	0.005	0.003
u(xi)	0.064	0.078	0.048	0.053	0.048	0.220	0.010	0.029	0.068
U(xi)	0.128	0.155	0.096	0.106	0.097	0.441	0.019	0.058	0.136

Figure 23: Reported values for CO run 4.

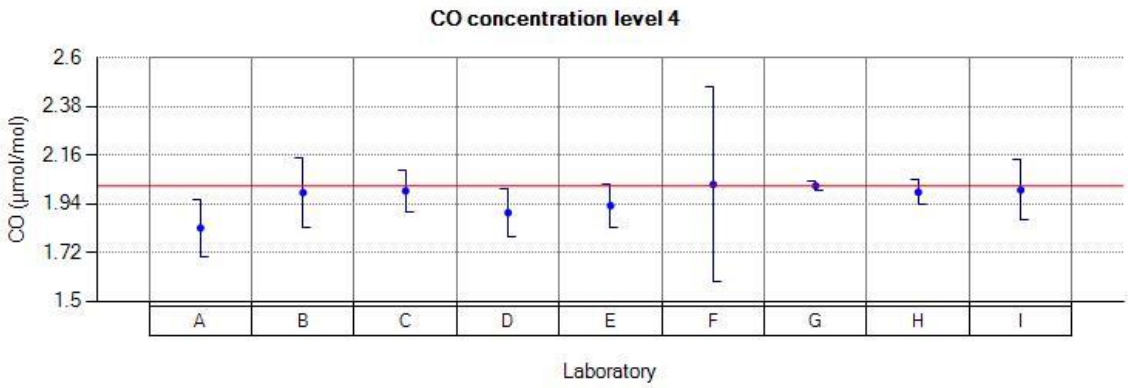
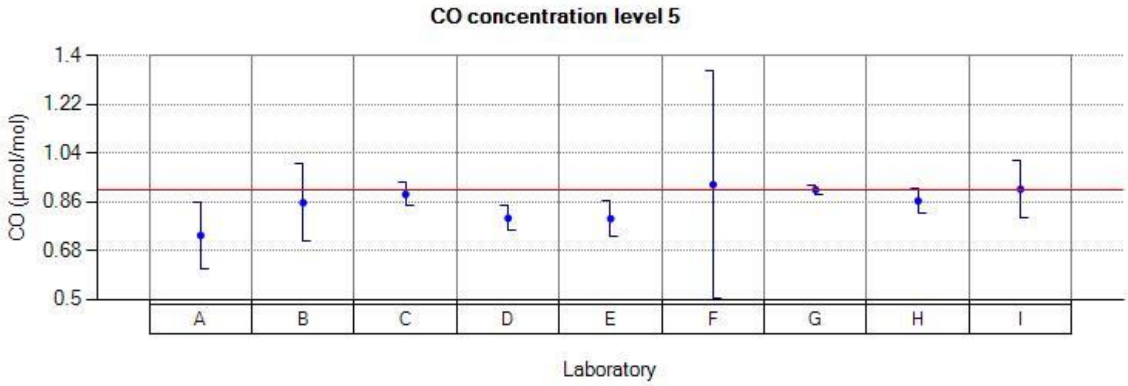


Table 22: Reported values for CO run 5.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	0.738	0.864	0.890	0.800	0.800	0.924	0.906	0.868	0.908
xi, 2	0.738	0.854	0.889	0.800	0.798	0.925	0.904	0.859	0.910
xi, 3	0.732	0.854	0.886	0.800	0.796	0.924	0.905	0.865	0.903
xi	0.736	0.857	0.888	0.800	0.798	0.924	0.905	0.864	0.907
si	0.003	0.006	0.002	0.000	0.002	0.001	0.001	0.005	0.004
u(xi)	0.063	0.071	0.021	0.022	0.033	0.209	0.009	0.024	0.054
U(xi)	0.125	0.142	0.042	0.045	0.067	0.418	0.018	0.047	0.108

Figure 24: Reported values for CO run 5.



Reported values for O_3

Table 23: Reported values for O_3 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	K
xi, 1	-0.89	-0.44	0.70	0.00	0.11	0.16	-0.08	-0.03	0.02	-0.80
u(xi)	0.71	0.63		0.00	0.60	0.50	0.24	0.70	0.60	0.47
U(xi)	1.42	1.26		0.00	1.20	1.01	0.48	1.40	1.20	0.94

Figure 25: Reported values for O_3 run 0.

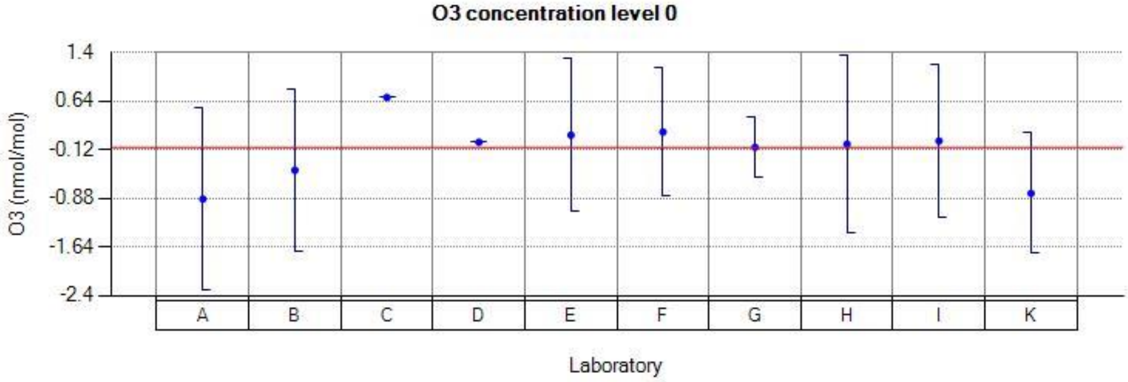


Table 24: Reported values for O_3 run 1.

	laboratories									
values	A	B	C	D	E	F	G	H	I	K
xi, 1	62.10	64.91	64.54	64.75	63.49	63.07	63.28	63.52	63.23	61.67
xi, 2	62.09	65.05	64.56	65.60	63.53	63.14	63.23	63.46	63.18	61.88
xi, 3	62.05	65.03	64.42	65.80	63.37	63.06	63.04	63.28	62.94	61.78
xi	62.08	64.99	64.50	65.38	63.46	63.09	63.18	63.42	63.11	61.77
si	0.02	0.07	0.07	0.55	0.08	0.04	0.12	0.12	0.15	0.10
u(xi)	1.46	1.61	1.46	1.20	1.07	1.45	0.52	1.01	1.24	0.50
U(xi)	2.92	3.22	2.92	2.41	2.15	2.89	1.03	2.02	2.47	1.00

Figure 26: Reported values for O_3 run 1.

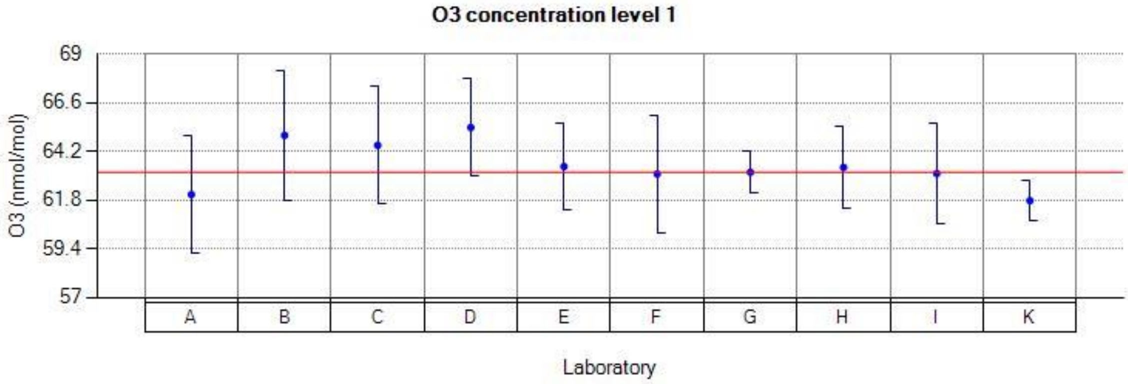


Table 25: Reported values for O_3 run 2.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	17.38	18.32	19.04	18.60	18.71	18.27	18.08	18.23	17.99	17.44
xi, 2	17.37	18.37	19.01	18.60	18.81	18.28	18.06	18.17	17.95	17.48
xi, 3	17.36	18.31	19.04	18.70	18.74	18.29	18.03	18.16	17.90	17.55
xi	17.37	18.33	19.03	18.63	18.75	18.28	18.05	18.18	17.94	17.49
si	0.01	0.03	0.01	0.05	0.05	0.01	0.02	0.03	0.04	0.05
u(xi)	0.79	0.75	0.96	0.31	0.66	0.77	0.24	0.73	0.77	0.47
U(xi)	1.58	1.51	1.92	0.62	1.32	1.55	0.48	1.46	1.54	0.94

Figure 27: Reported values for O_3 run 2.

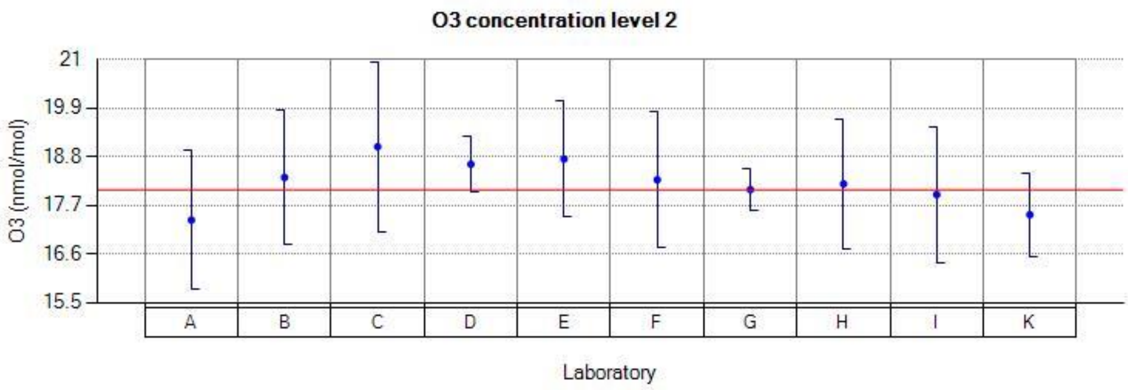


Table 26: Reported values for O_3 run 3.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	32.88	34.42	34.69	35.10	34.16	33.76	33.52	33.74	33.32	32.73
xi, 2	32.91	34.49	34.70	35.40	34.43	33.80	33.51	33.75	33.33	32.72
xi, 3	32.90	34.51	34.68	35.65	34.05	33.81	33.50	33.76	33.38	32.83
xi	32.89	34.47	34.69	35.38	34.21	33.79	33.51	33.75	33.34	32.76
si	0.01	0.04	0.01	0.27	0.19	0.02	0.01	0.01	0.03	0.06
u(xi)	0.98	1.01	1.13	0.64	0.77	1.01	0.31	0.80	0.92	0.48
U(xi)	1.96	2.01	2.26	1.28	1.54	2.01	0.62	1.60	1.84	0.96

Figure 28: Reported values for O_3 run 3.

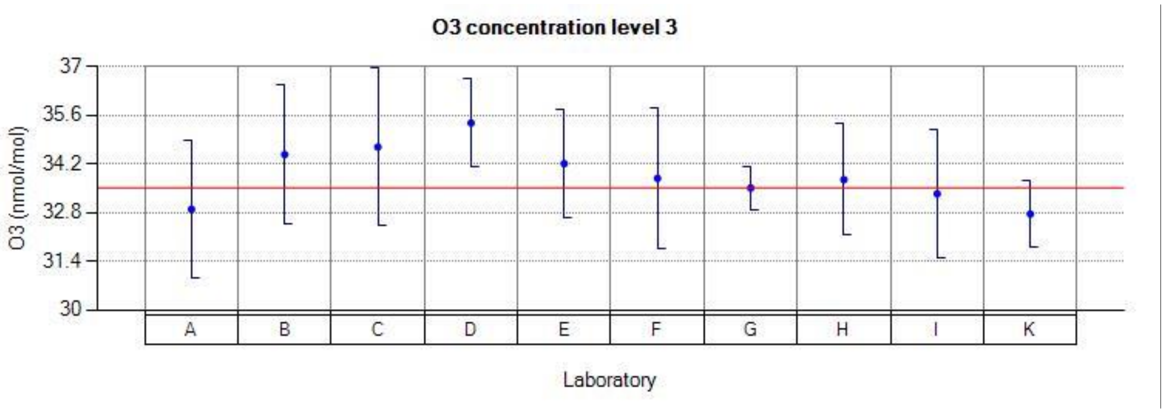


Table 27: Reported values for O_3 run 4.

values	A	B	C	D	E	F	G	H	I	K
	laboratories									
xi, 1	113.21	118.01	116.06	122.85	114.77	114.40	113.88	114.39	113.61	112.44
xi, 2	113.47	118.34	116.22	123.30	114.95	114.63	114.03	114.61	113.83	112.71
xi, 3	113.53	118.53	116.39	124.00	114.75	114.84	114.16	114.55	113.95	112.93
xi	113.40	118.29	116.22	123.38	114.82	114.62	114.02	114.51	113.79	112.69
si	0.17	0.26	0.16	0.58	0.11	0.22	0.14	0.11	0.17	0.24
u(xi)	2.43	2.77	2.03	2.10	1.71	2.22	0.91	1.49	1.72	0.57
U(xi)	4.86	5.55	4.06	4.19	3.42	4.44	1.83	2.98	3.44	1.14

Figure 29: Reported values for O_3 run 4.

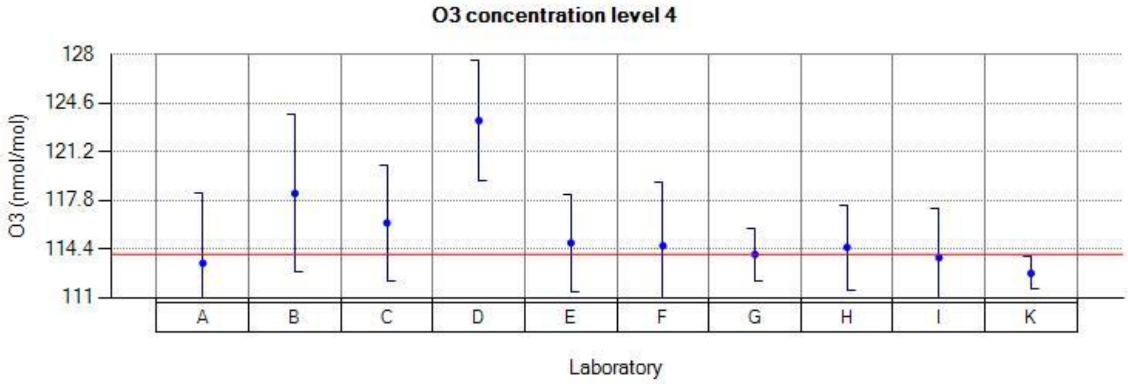
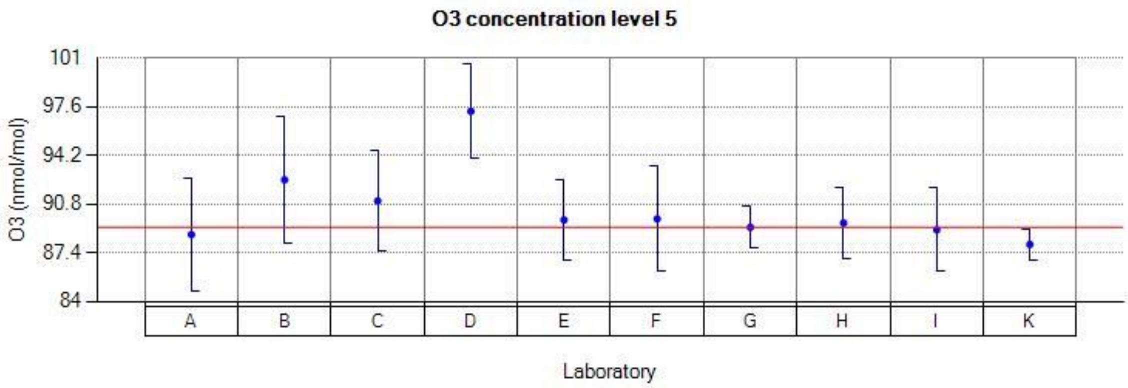


Table 28: Reported values for O_3 run 5.

values	A	B	C	D	E	F	G	H	I	K
	laboratories									
xi, 1	88.55	92.36	90.97	96.80	89.25	89.66	89.15	89.40	89.01	87.84
xi, 2	88.73	92.56	91.04	97.60	90.07	89.81	89.19	89.53	89.01	88.06
xi, 3	88.75	92.61	91.08	97.50	89.78	89.84	89.21	89.53	89.00	88.06
xi	88.67	92.51	91.03	97.30	89.70	89.77	89.18	89.48	89.00	87.98
si	0.11	0.13	0.05	0.43	0.41	0.09	0.03	0.07	0.00	0.12
u(xi)	1.96	2.20	1.75	1.65	1.39	1.85	0.71	1.24	1.47	0.53
U(xi)	3.92	4.41	3.50	3.30	2.78	3.69	1.43	2.49	2.94	1.06

Figure 30: Reported values for O_3 run 5.



Reported values for NO

Table 29: Reported values for NO run 0.

values	A	B	C	D	E	F	G	H	I	K
	laboratories									
xi, 1	-0.02	0.88	-0.56	-0.40	0.08	0.01	-0.07	-0.15	0.16	0.08
u(xi)	0.58	0.68		0.00	0.16	0.50	0.71	0.47	0.32	0.63
U(xi)	1.16	1.35		0.01	0.32	1.00	1.42	0.95	0.63	1.26

Figure 31: Reported values for NO run 0.

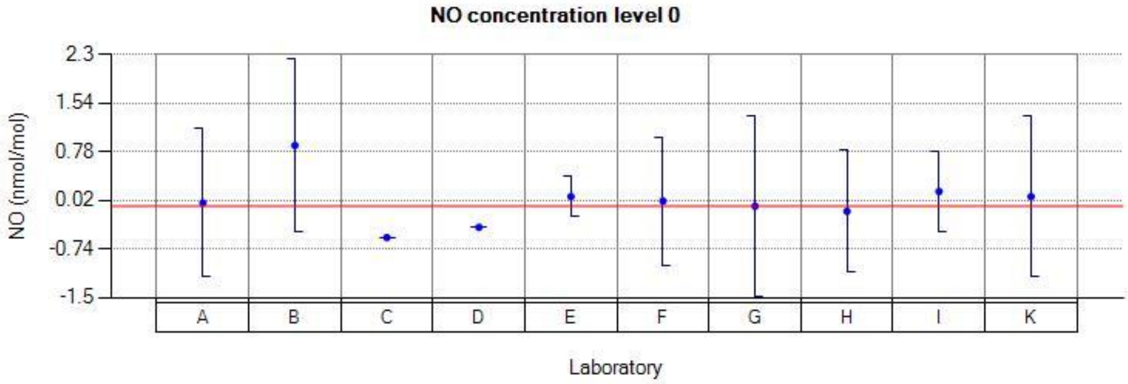


Table 30: Reported values for NO run 1.

values	A	B	C	D	E	F	G	H	I	K
	laboratories									
xi, 1	137.94	136.67	137.36	133.90	137.23	137.55	137.99	137.52	137.07	131.43
xi, 2	137.98	136.42	137.27	133.85	137.40	137.57	138.01	137.45	136.91	131.47
xi, 3	138.01	136.86	137.25	131.10	137.52	137.54	137.88	137.70	136.89	131.45
xi	137.97	136.65	137.29	132.95	137.38	137.55	137.96	137.55	136.95	131.45
si	0.03	0.22	0.05	1.60	0.14	0.01	0.07	0.12	0.09	0.02
u(xi)	1.21	2.34	2.49	4.12	1.50	3.25	1.14	1.75	2.77	5.98
U(xi)	2.42	4.67	4.98	8.23	3.01	6.50	2.28	3.49	5.54	11.96

Figure 32: Reported values for NO run 1.

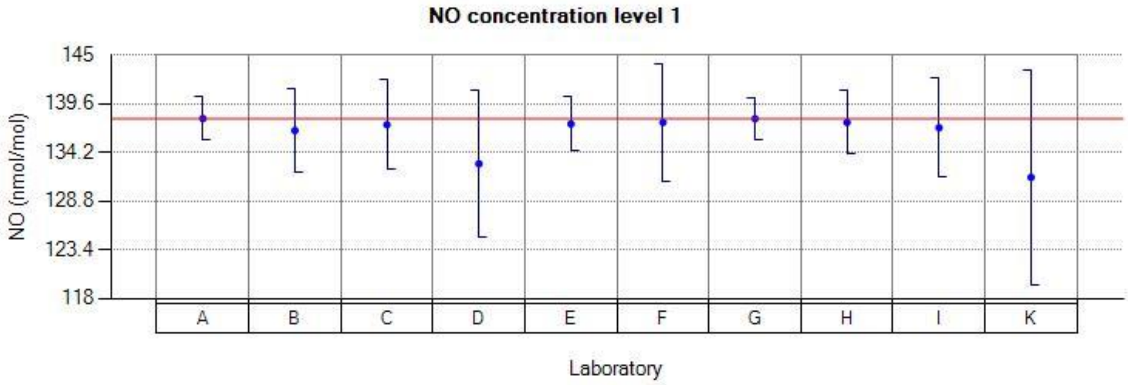


Table 31: Reported values for NO run 2.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	72.59	71.94	72.11	69.95	72.47	72.75	72.14	72.59	72.46	68.36
xi, 2	72.82	71.88	72.30	70.05	72.74	72.89	72.29	72.89	72.72	68.55
xi, 3	72.94	72.63	72.44	70.00	72.85	73.15	72.36	72.77	72.82	68.65
xi	72.78	72.15	72.28	70.00	72.68	72.93	72.26	72.75	72.66	68.52
si	0.17	0.41	0.16	0.05	0.19	0.20	0.11	0.15	0.18	0.14
u(xi)	0.81	1.36	1.33	2.15	0.80	1.96	0.85	1.00	1.66	3.16
U(xi)	1.61	2.72	2.66	4.30	1.61	3.92	1.71	2.00	3.31	6.32

Figure 33: Reported values for NO run 2.

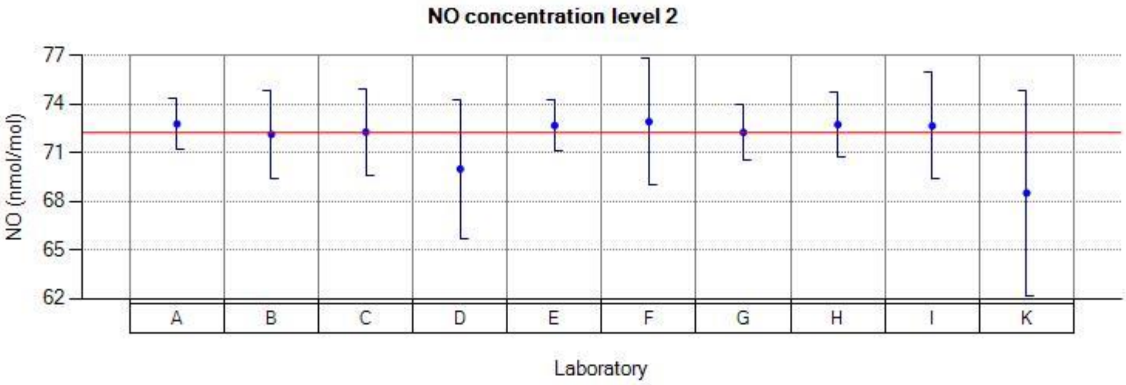


Table 32: Reported values for NO run 3.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	36.14	36.92	35.55	34.55	35.75	35.91	35.66	35.88	35.70	33.51
xi, 2	36.16	36.43	35.74	34.25	35.82	35.78	35.64	36.01	35.71	33.41
xi, 3	36.19	36.42	35.82	34.50	35.76	35.93	35.66	36.06	35.73	33.56
xi	36.16	36.59	35.70	34.43	35.77	35.87	35.65	35.98	35.71	33.49
si	0.02	0.28	0.13	0.16	0.03	0.08	0.01	0.09	0.01	0.07
u(xi)	0.64	0.90	0.69	1.07	0.42	1.22	0.75	0.51	1.10	1.64
U(xi)	1.28	1.81	1.38	2.14	0.84	2.43	1.50	1.02	2.19	3.28

Figure 34: Reported values for NO run 3.

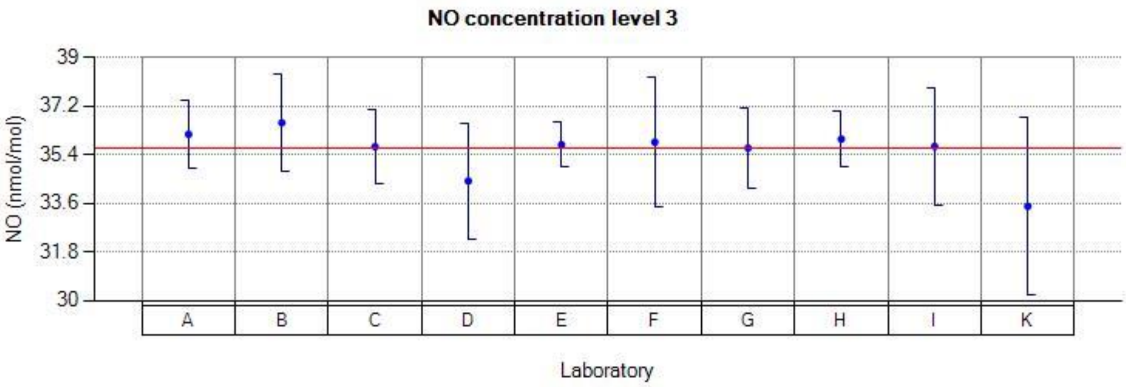


Table 33: Reported values for NO run 4.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	17.41	18.48	17.18	16.30	17.30	17.31	17.04	17.42	17.40	16.13
xi, 2	17.46	18.50	17.15	16.65	17.42	17.29	17.08	17.44	17.38	16.06
xi, 3	17.44	18.50	17.17	16.00	17.47	17.35	17.09	17.40	17.42	15.90
xi	17.43	18.49	17.16	16.31	17.39	17.31	17.07	17.42	17.40	16.03
si	0.02	0.01	0.01	0.32	0.08	0.03	0.02	0.02	0.02	0.11
u(xi)	0.59	0.74	0.37	0.60	0.25	0.85	0.72	0.46	0.76	0.96
U(xi)	1.18	1.48	0.74	1.19	0.50	1.69	1.44	0.91	1.52	1.92

Figure 35: Reported values for NO run 4.

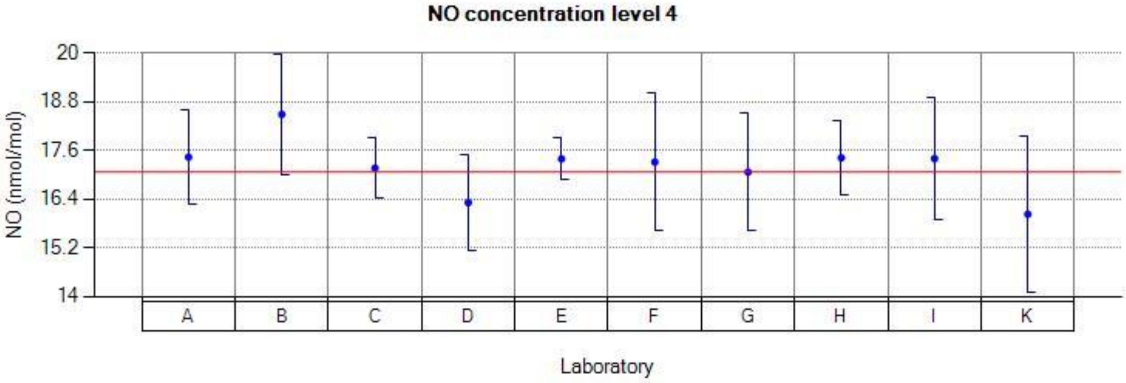


Table 34: Reported values for NO run 5.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	66.99	66.01	66.39	63.65	66.50	66.49	66.01	66.84	66.12	62.48
xi, 2	66.98	66.32	66.50	63.75	66.38	66.55	65.98	66.79	66.10	62.69
xi, 3	67.06	66.24	66.41	63.90	66.31	66.55	65.99	66.78	66.07	62.65
xi	67.01	66.19	66.43	63.76	66.39	66.53	65.99	66.80	66.09	62.60
si	0.04	0.16	0.05	0.12	0.09	0.03	0.01	0.03	0.02	0.11
u(xi)	0.78	1.28	1.22	1.96	0.74	1.83	0.83	0.87	1.56	2.90
U(xi)	1.55	2.55	2.44	3.92	1.48	3.66	1.67	1.73	3.11	5.80

Figure 36: Reported values for NO run 5.

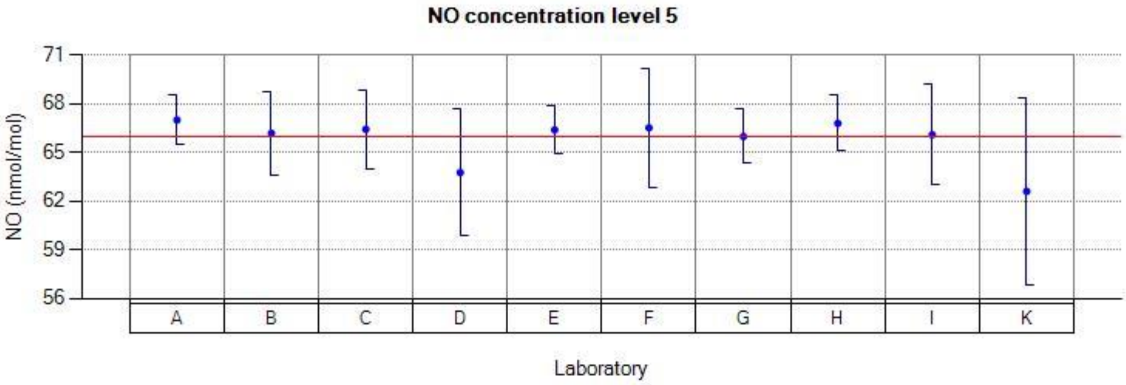


Table 35: Reported values for NO run 6.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	27.30	27.76	26.92	25.75	27.27	27.22	26.68	27.31	27.25	25.07
xi, 2	27.43	28.06	26.97	25.60	27.19	27.36	26.77	27.46	27.35	25.26
xi, 3	27.53	28.07	27.12	26.15	27.32	27.53	26.90	27.60	27.43	25.42
xi	27.42	27.96	27.00	25.83	27.26	27.37	26.78	27.45	27.34	25.25
si	0.11	0.17	0.10	0.28	0.06	0.15	0.11	0.14	0.09	0.17
u(xi)	0.61	0.82	0.53	0.84	0.33	1.05	0.74	0.41	0.97	1.31
U(xi)	1.23	1.63	1.06	1.69	0.67	2.09	1.47	0.82	1.94	2.62

Figure 37: Reported values for NO run 6.

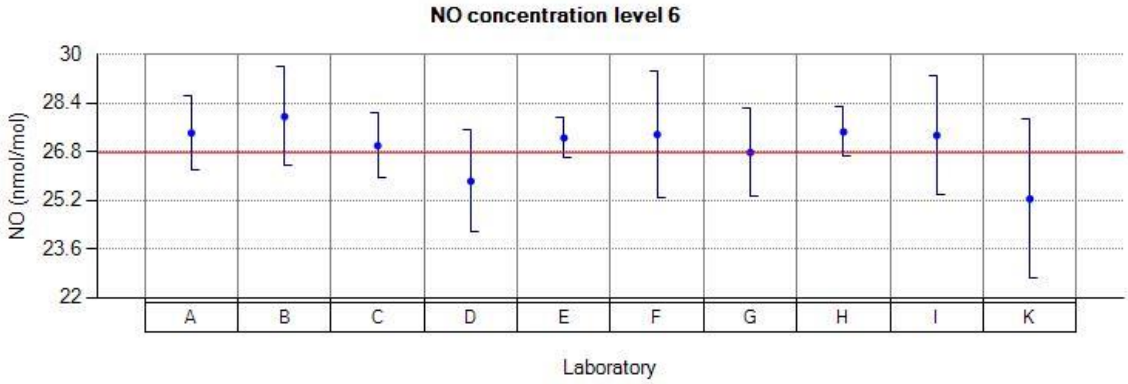


Table 36: Reported values for NO run 7.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	499.02	485.18	489.55	476.90	493.85	495.38	493.74	496.98	492.35	479.64
xi, 2	499.45	486.31	489.95	477.25	493.83	495.95	494.01	497.46	492.69	480.11
xi, 3	499.52	487.03	489.76	477.10	494.64	496.08	494.39	497.76	493.00	480.35
xi	499.33	486.17	489.75	477.08	494.10	495.80	494.04	497.40	492.68	480.03
si	0.27	0.93	0.20	0.17	0.46	0.37	0.32	0.39	0.32	0.36
u(xi)	3.90	7.99	8.83	14.65	5.38	10.42	3.25	6.23	8.71	21.72
U(xi)	7.79	15.97	17.66	29.31	10.77	20.83	6.50	12.46	17.42	43.44

Figure 38: Reported values for NO run 7.

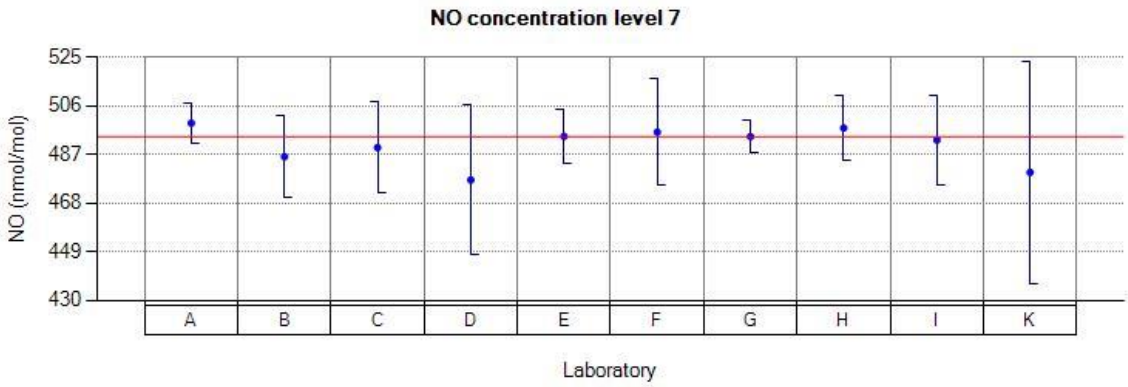


Table 37: Reported values for NO run 8.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	388.43	379.11	381.84	371.05	385.40	387.78	384.68	388.25	385.45	372.38
xi, 2	387.86	378.97	381.16	370.95	384.62	387.28	384.72	387.98	385.31	371.67
xi, 3	387.18	379.97	381.17	371.80	384.65	386.92	385.52	387.60	385.04	371.46
xi	387.82	379.35	381.39	371.26	384.89	387.32	384.97	387.94	385.26	371.83
si	0.62	0.54	0.39	0.46	0.44	0.43	0.47	0.32	0.20	0.48
u(xi)	3.04	6.25	6.88	11.41	4.19	8.25	2.58	4.87	6.86	16.83
U(xi)	6.09	12.49	13.76	22.82	8.39	16.49	5.16	9.73	13.71	33.66

Figure 39: Reported values for NO run 8.

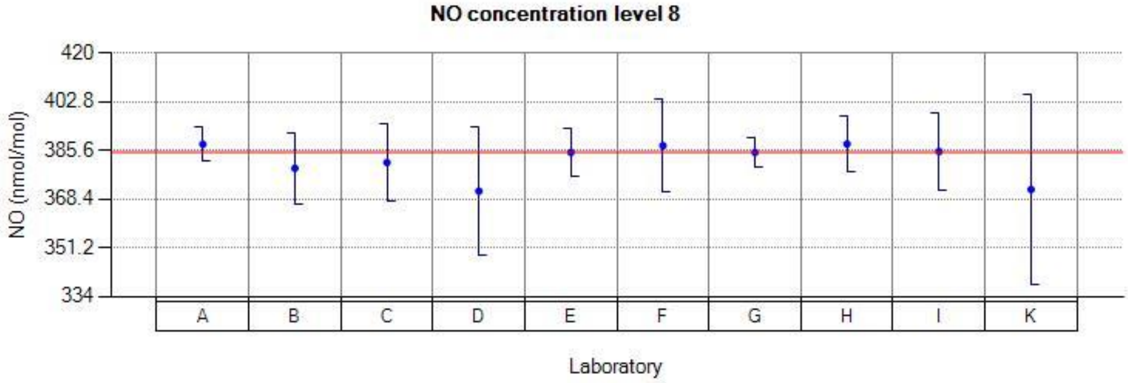


Table 38: Reported values for NO run 9.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	303.84	297.24	299.11	291.15	300.77	302.28	302.88	302.79	300.84	290.10
xi, 2	304.13	297.72	299.42	291.65	301.56	302.66	302.92	303.34	301.11	290.69
xi, 3	304.50	298.03	299.62	291.50	301.86	302.74	303.03	303.63	301.23	290.96
xi	304.15	297.66	299.38	291.43	301.39	302.56	302.94	303.25	301.06	290.58
si	0.33	0.39	0.25	0.25	0.56	0.24	0.07	0.42	0.20	0.44
u(xi)	2.41	4.92	5.41	8.95	3.29	6.55	2.07	3.80	5.44	13.16
U(xi)	4.82	9.84	10.82	17.91	6.58	13.10	4.14	7.60	10.88	26.32

Figure 40: Reported values for NO run 9.

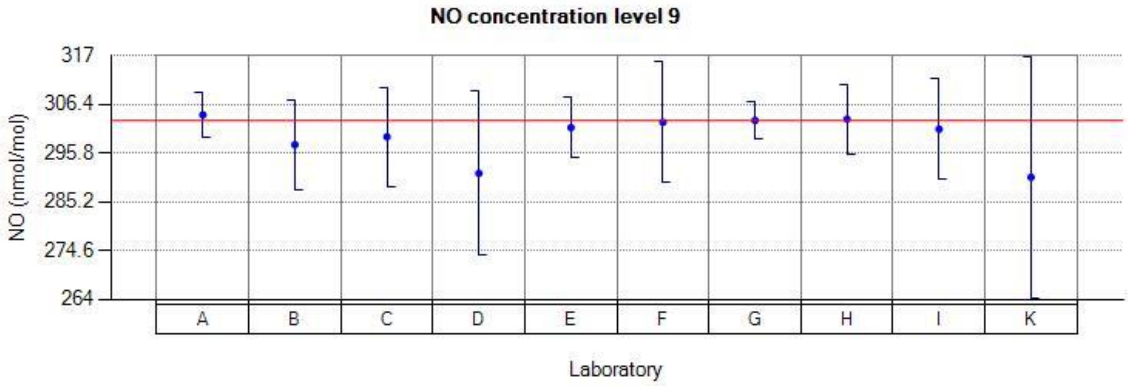
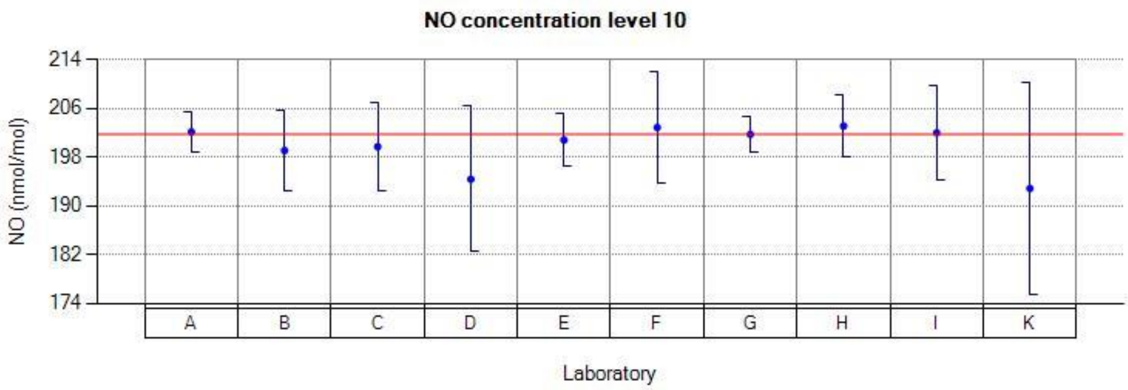


Table 39: Reported values for NO run 10.

values	A	B	C	D	E	F	G	H	I	K
	laboratories									
xi, 1	202.50	198.94	199.92	194.45	201.12	203.12	201.92	203.31	202.28	193.26
xi, 2	202.03	199.23	199.78	194.50	200.77	202.85	201.58	203.09	201.88	192.81
xi, 3	201.98	199.15	199.54	194.25	200.62	202.70	201.78	202.98	201.89	192.54
xi	202.17	199.10	199.74	194.40	200.83	202.89	201.76	203.12	202.01	192.87
si	0.28	0.15	0.19	0.13	0.25	0.21	0.17	0.16	0.22	0.36
u(xi)	1.66	3.33	3.62	5.97	2.19	4.56	1.49	2.57	3.91	8.75
U(xi)	3.32	6.66	7.24	11.94	4.39	9.12	2.97	5.13	7.82	17.50

Figure 41: Reported values for NO run 10.



Reported values for NO_2

Table 40: Reported values for NO_2 run 0.

	laboratories									
values	A	B	C	D	E	F	G	H	I	K
xi, 1	-0.08	-0.21	0.01	1.30	0.11	-0.14	0.03	-0.03	0.20	0.03
u(xi)	0.58	0.68		0.01	0.18	0.50	0.71	0.77	0.32	0.63
U(xi)	1.16	1.35		0.01	0.36	0.99	1.43	1.54	0.63	1.26

Figure 42: Reported values for NO_2 run 0.

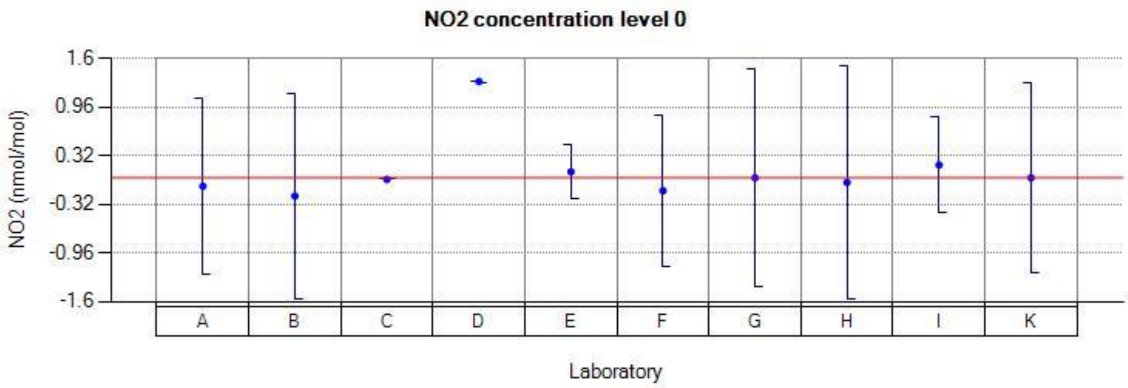


Table 41: Reported values for NO_2 run 2.

	laboratories									
values	A	B	C	D	E	F	G	H	I	K
xi, 1	66.23	64.06	67.25	62.15	65.96	65.01	66.18	65.89	64.82	62.35
xi, 2	66.02	63.94	66.91	62.65	65.44	64.85	66.02	65.68	64.55	62.24
xi, 3	65.99	63.90	66.84	62.25	65.21	64.75	65.83	65.47	64.44	61.78
xi	66.08	63.96	67.00	62.35	65.53	64.87	66.01	65.68	64.60	62.12
si	0.13	0.08	0.21	0.26	0.38	0.13	0.17	0.21	0.19	0.30
u(xi)	1.36	1.79	1.80	17.93	1.18	1.80	0.98	1.03	1.55	2.88
U(xi)	2.71	3.57	3.60	35.87	2.36	3.59	1.97	2.06	3.10	5.76

Figure 43: Reported values for NO_2 run 2.

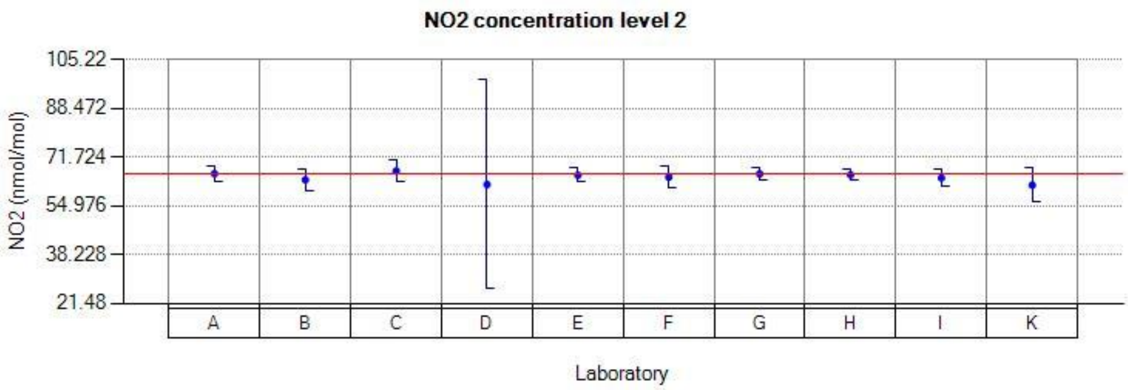


Table 42: Reported values for NO_2 run 4.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	18.77	17.86	19.14	17.30	18.78	18.53	18.77	18.67	18.49	17.40
xi, 2	18.72	18.12	19.07	17.10	18.57	18.59	18.74	18.77	18.44	17.47
xi, 3	18.73	17.97	19.19	17.55	18.75	18.46	18.72	18.70	18.43	17.43
xi	18.74	17.98	19.13	17.31	18.70	18.52	18.74	18.71	18.45	17.43
si	0.02	0.13	0.06	0.22	0.11	0.06	0.02	0.05	0.03	0.03
u(xi)	0.67	0.82	0.55	4.99	0.38	0.87	0.74	0.77	0.77	1.01
U(xi)	1.35	1.64	1.10	9.97	0.76	1.74	1.48	1.53	1.53	2.02

Figure 44: Reported values for NO_2 run 4.

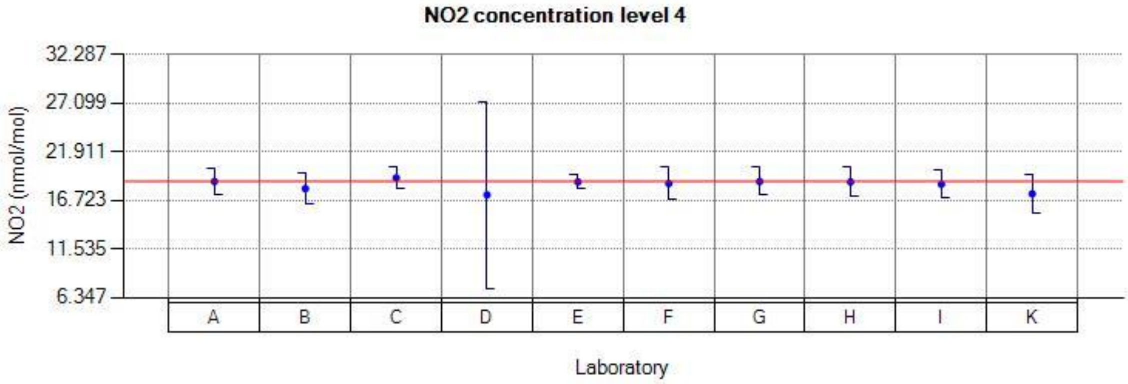


Table 43: Reported values for NO_2 run 6.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	39.85	37.94	40.53	36.80	39.52	39.01	39.50	39.64	38.96	37.20
xi, 2	39.68	38.11	40.30	37.10	39.39	38.97	39.41	39.60	38.94	37.14
xi, 3	39.62	38.33	40.19	36.55	39.41	38.83	39.28	39.42	38.72	36.74
xi	39.71	38.12	40.34	36.81	39.44	38.93	39.39	39.55	38.87	37.02
si	0.11	0.19	0.17	0.27	0.07	0.09	0.11	0.11	0.13	0.25
u(xi)	0.94	1.19	1.10	10.59	0.72	1.28	0.81	0.60	1.11	1.79
U(xi)	1.87	2.39	2.20	21.19	1.45	2.56	1.61	1.20	2.21	3.58

Figure 45: Reported values for NO_2 run 6.

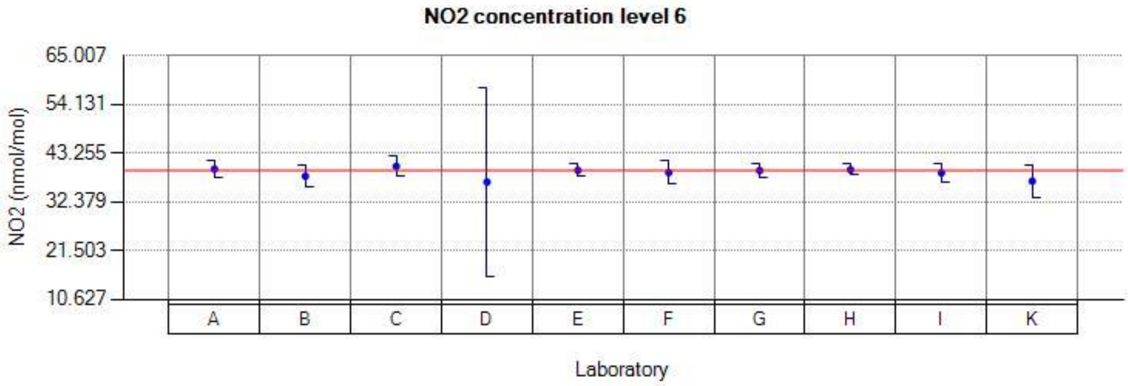


Table 44: Reported values for NO_2 run 8.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	118.07	113.54	123.24	108.55	117.90	117.89	117.13	117.64	114.99	111.07
xi, 2	118.34	114.66	123.94	108.90	118.73	118.84	117.89	117.92	115.19	111.90
xi, 3	118.72	112.92	123.83	108.10	118.35	119.69	118.01	118.25	115.41	112.15
xi	118.37	113.70	123.67	108.51	118.32	118.80	117.67	117.93	115.19	111.70
si	0.32	0.88	0.37	0.40	0.41	0.90	0.47	0.30	0.21	0.56
u(xi)	2.27	3.02	3.30	31.21	2.11	2.88	2.07	1.57	2.59	5.09
U(xi)	4.54	6.03	6.60	62.43	4.22	5.75	4.14	3.13	5.17	10.18

Figure 46: Reported values for NO_2 run 8.

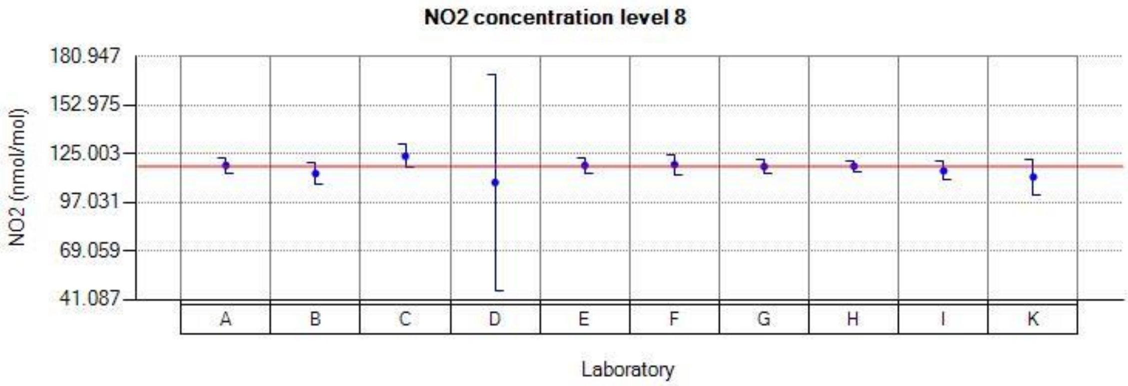
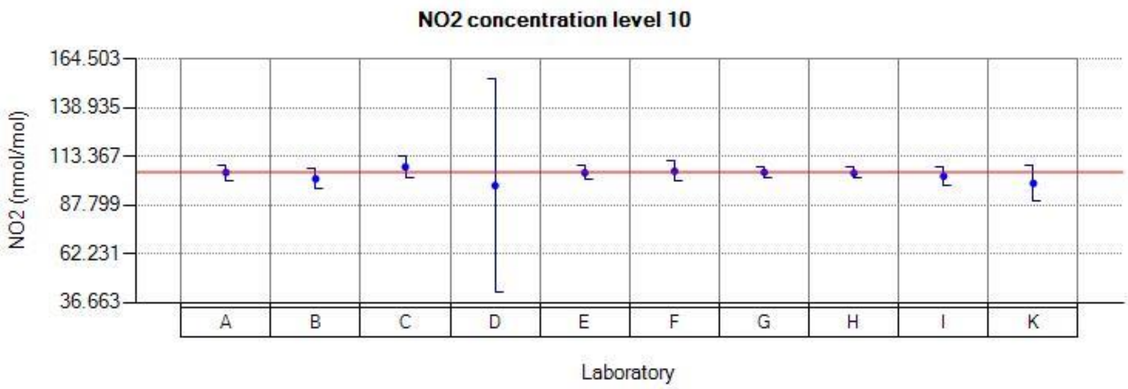


Table 45: Reported values for NO_2 run 10.

values	laboratories									
	A	B	C	D	E	F	G	H	I	K
xi, 1	104.86	101.16	107.59	98.20	104.73	105.23	104.79	104.48	102.78	99.01
xi, 2	105.01	101.35	107.86	98.10	104.83	105.63	105.09	104.75	103.19	99.37
xi, 3	105.18	102.38	108.29	97.95	105.07	106.05	105.44	104.93	103.28	99.48
xi	105.01	101.63	107.91	98.08	104.87	105.63	105.10	104.72	103.08	99.28
si	0.16	0.65	0.35	0.12	0.17	0.41	0.32	0.22	0.26	0.24
u(xi)	2.03	2.71	2.88	28.21	1.88	2.61	1.49	1.41	2.33	4.54
U(xi)	4.07	5.42	5.76	56.42	3.76	5.23	2.98	2.81	4.66	9.08

Figure 47: Reported values for NO_2 run 10.



Annex B: precision of standardised measurement methods

For the main purpose of monitoring trends between different ILC undertaken by ERLAP, the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [2], [3], [4] and [5] as implemented by NRLs, was evaluated.

Applied methodology is described in ISO 5725-1, 5725-2 and 5725-6 [14], [15] and [16]. The precision experiment has involved a total of nine laboratories, the actual number of labs (***p_j***) is reported in Table 46. Six concentration levels (for run 0 only one value is requested so repeatability cannot be evaluated) were tested for O_3, CO, SO_2 and NO_2, and eleven for NO. Outlier tests were performed and results are reported in Annex D.

The repeatability standard deviation (***s_r***) was calculated in accordance with ISO 5725-6 as the square root of average within-laboratory variance. The repeatability limit (***r***) is calculated using Equation 6 [16]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval that should not be exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_r$$ **Equation 6**

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-6 as the square root of sum of repeatability and between-laboratory variance. The reproducibility limit (R) is calculated using Equation 7 [16]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, which should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_R$$ **Equation 7**

The repeatability standard deviation was evaluated with (***p_j *(3-1)***) degrees of freedom (ν) and reproducibility standard deviation with (***p_j-1***) degrees of freedom. The corresponding critical range student factors ($t_{\alpha,\nu}$) are reported in Table 46.

Table 46: Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	9	2,101	2,306
NO	1,2,3,4,5,6,7,8,9,10	10	2,086	2,262
NO_2	2,4,6,8,10	10	2,086	2,262
O_3	1,2,3,4,5	10	2,086	2,262
SO_2	1,2,3,4,5	9	2,101	2,306

The repeatability (***r***) and reproducibility (***R***) limits of measurement methods are presented from Table 47 to Table 51 and from Figure 48 to Figure 52.

It is also reported the 'reproducibility from common criteria (R (from σ_p))' calculated by substituting s_R in Equation 7 with a 'standard deviation for proficiency assessment' (see Table 4). Comparison between R and R (from σ_p) serves to indicate that σ_p is realistic [13] or from the other point of view, that the general methodology implemented by NRLs is appropriate for $\boldsymbol{\sigma_p}$.

Table 47: The R and r of SO_2 standard measurement method.

SO_2 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0,0		2,5	
9,8	0,3	2,1	
17,8	0,2	2,3	
37,5	0,4	3,2	
63,8	0,5	4,7	
121,4	0,9	8,1	6,7%

Figure 48: The R and r of SO_2 standard measurement method as a function of concentration.

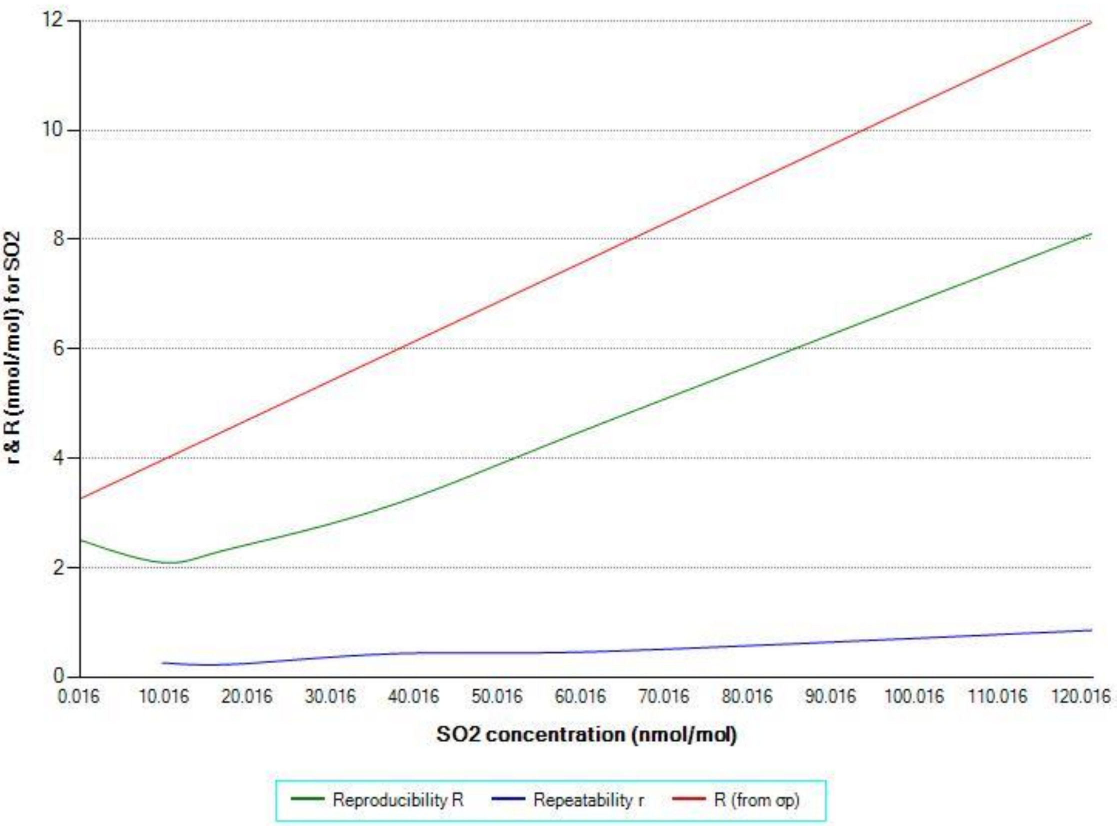


Table 48: The R and r of CO standard measurement method.

CO data (µmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
-0,040		0,162	
0,853	0,01	0,206	
1,967	0,009	0,215	
2,789	0,053	0,171	
5,049	0,009	0,238	
8,607	0,014	0,285	3,3%

Figure 49: The R and r of CO standard measurement method as a function of concentration.

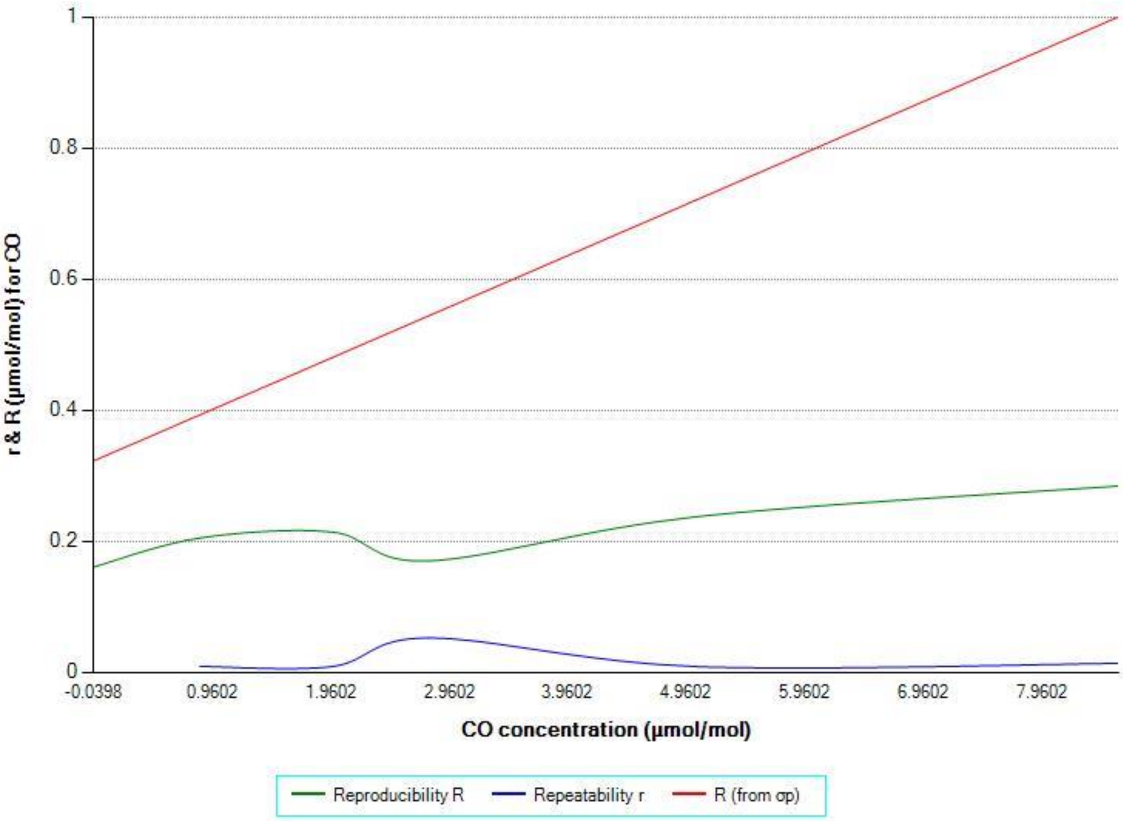


Table 49: The R and r of O_3 standard measurement method.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
-0,1		1,5	
18,2	0,1	1,7	
33,9	0,3	2,6	
63,5	0,6	3,8	
90,5	0,6	8,7	
115,6	0,7	10,1	8,7%

Figure 50: The R and r of O_3 standard measurement method as a function of concentration.

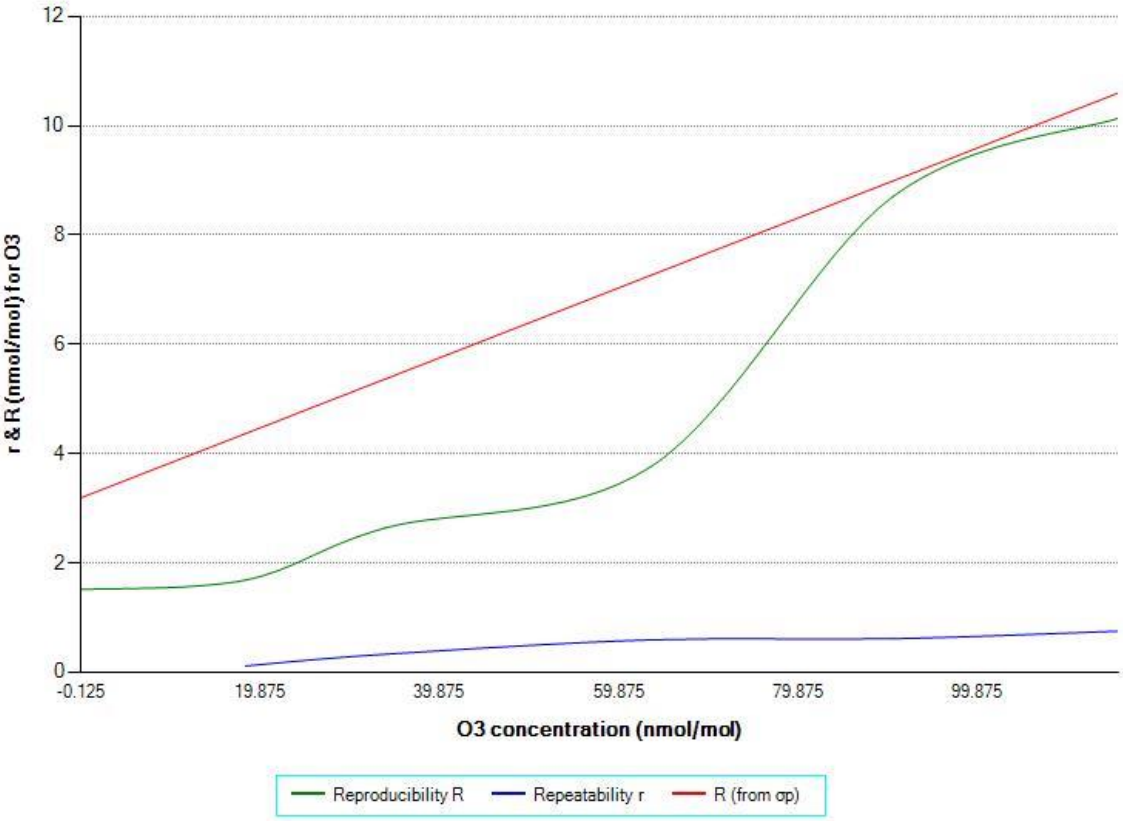


Table 50: The R and r of NO standard measurement method.

NO data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0,0		1,2	
17,2	0,3	2,2	
27,0	0,5	2,7	
35,5	0,4	2,9	
65,8	0,3	4,6	
71,9	0,6	4,7	
136,4	1,5	7,4	
199,9	0,7	11,4	
299,4	1,0	15,5	
382,2	1,3	20,0	
490,6	1,3	23,7	4,8%

Figure 51: The R and r of NO standard measurement method as a function of concentration.

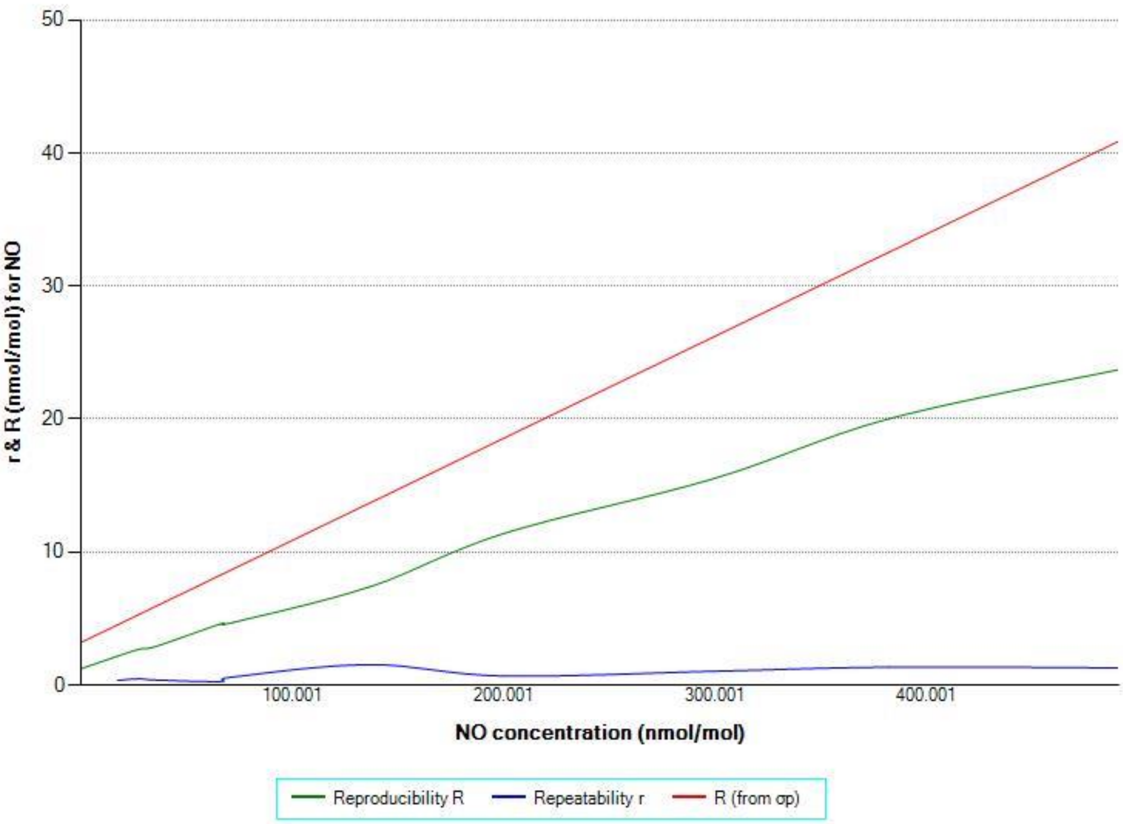
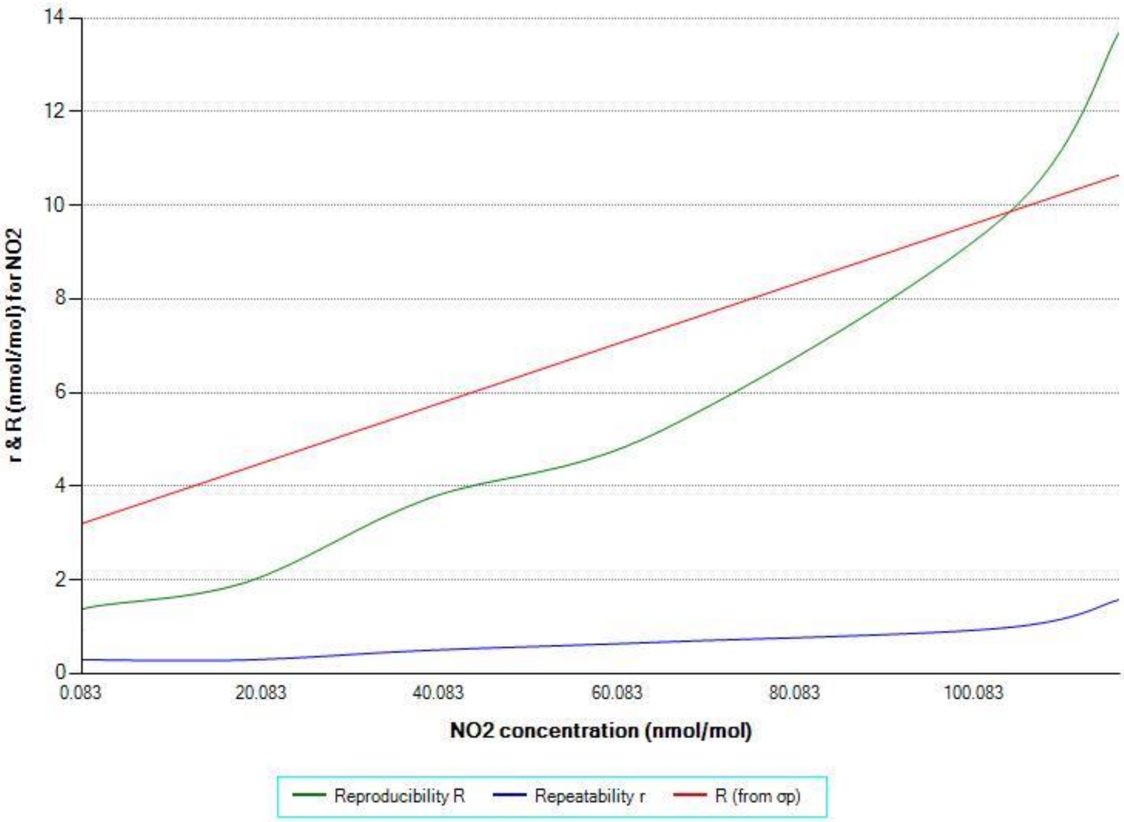


Table 51: The R and r of NO_2 standard measurement method.

NO_2 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0,1		1,4	
18,4	0,3	1,9	
38,8	0,5	3,7	
64,8	0,7	5,2	
103,5	1,0	9,8	
116,4	1,6	13,7	11,8%

Figure 52: The R and r of NO_2 standard measurement method as a function of concentration.



Annex C: scrutiny of results for consistency and outlier test

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures.

For that reason, a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or the calculation, wrong averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure were carried out tests for data consistency and statistical outliers as described in ISO 5725-2.

Laboratories showing some form of statistical inconsistency were requested to investigate the cause of discrepancies.

Laboratories were allowed to correct their results in case of identification of exceptional errors. Subsequently, data were considered definitive and z'-scores calculation was performed to estimate outliers.

Statistical outliers obtained at this stage are not considered as extraordinary errors but due to significant difference in participant's standard operating procedure.

The precision of standardised measurement methods reported in 0 are calculated using the database without outliers.

According to z'-score calculation, results between |2| and |3| are considered stragglers and they deserve a specific check. Four values were evaluated as stragglers: level 4 and 5 of O_3 and level 8 and 10 of NO_2, all for Laboratory D.

During this ILC, no outliers were identified.

Annex D: Confidentiality

Results of the ILC are published according to the agreements included in the document AQUILA-N37 [12] approved by all NRL.

In order to ensure confidentiality of the laboratories information, ERLAP guarantees the submitted data as follows:

- Any administrative information provided by the laboratory is confidential and cannot be communicated to a third party.
- Access to ERLAP facilities is allowed only to members of the Unit JRC-C5 and authorized persons (cleaning staff, maintenance staff, safety and security staff etc.)
- Confidential passwords to access the web application for data submission are sent once the registration to ILC is completed. Confidential passwords allow access to the WEB interface and to on-line questionnaire. Passwords are valid until the ILC is closed. Laboratories can change their password online.
- The form LAB-REC-2000 (Confidentiality involvement form) is asked to be signed by the participants during their first participation to an ILC organized by ERLAP.

Annex E: Accreditation certificates

ACCREDIA
L'ENTE ITALIANO DI ACCREDITAMENTO

Membro degli Accordi di Mutuo Riconoscimento EA, IAF e ILAC
Signatory of EA, IAF and ILAC Mutual Recognition Agreements

CERTIFICATO DI ACCREDITAMENTO
Accreditation Certificate

ACCREDITAMENTO N. / *ACCREDITATION N.* **0018P** REV. **00**

EMESSO DA / ISSUED BY **DIPARTIMENTO LABORATORI DI PROVA**

SI DICHIARA CHE / *WE DECLARE THAT* **European Reference Laboratory for air Pollution (ERLAP)**
Sede/Headquarters:
- Via E. Fermi 2749 - 21027 Ispra VA

È CONFORME AI REQUISITI DELLA NORMA UNI CEI EN ISO/IEC 17043:2010

MEETS THE REQUIREMENTS OF THE STANDARD *ISO/IEC 17043:2010*

MD-CA-01 rev. 03

QUALE **Organizzatori di prove valutative interlaboratorio**

AS ***Proficiency Testing Provider***

Data di 1ª emissione *1st issue date* **17-01-2019**	Data di modifica *Modification date* **17-01-2019**	Data di scadenza *Expiring date* **16-01-2023**
Dott.ssa Silvia Tramontin Il Direttore di Dipartimento *The Department Director*	Dott. Filippo Trifiletti Il Direttore Generale *The General Director*	Ing. Giuseppe Rossi Il Presidente *The President*

L'accreditamento attesta la competenza tecnica dell'Organizzazione relativamente al campo di accreditamento riportato nell'Elenco Schemi allegato al presente certificato di accreditamento.
Il presente certificato non è da ritenersi valido se non accompagnato dagli Elenchi Schemi, che possono variare nel tempo.
La vigenza dell'accreditamento può essere verificata sul sito web (www.accredia.it) o richiesta al Dipartimento di competenza.

The accreditation certifies the technical competence of the organisation limited to the scope detailed in the attached Enclosure. The present certificate is valid only if associated to the annexed schedule, that may vary in the time. Confirmation of the validity of accreditation can be verified on website www.accredia.it or by contacting the relevant Department.

pag. 1/1

ACCREDIA

Sede operativa e legale: Via Guglielmo Saliceto, 7/9 | 00161 Roma - Italy | Tel. +39 06 8440991 | Fax +39 06 8841199
info@accredia.it | www.accredia.it | Partita IVA - Codice Fiscale 10566361001

ACCREDIA
L'ENTE ITALIANO DI ACCREDITAMENTO

European Reference Laboratory for air Pollution (ERLAP) Via E. Fermi 2749 21027 Ispra VA	Numero di accreditamento: **0018 P** Sede **A**
	Revisione: **0** Data: **17/01/2019**
	pag. **1** di **1** UNI CEI EN ISO/IEC 17043:2010

ELENCO SCHEMI ACCREDITATI - CATEGORIA: 0

Codice identificativo	*Settore*	*Oggetto /Materiale/ Prodotto/Matrice*	*Misurando/ Proprietà misurata/ Grandezza*	*Tipologia*
	ambientale	purified ambient air	carbon monoxide	schema quantitativo
	ambientale	purified ambient air	nitrogen oxides	schema quantitativo
	ambientale	purified ambient air	ozone	schema quantitativo
	ambientale	purified ambient air	sulphur dioxide	schema quantitativo

Il QRcode consente di accedere direttamente al sito www.accredia.it per verificare la validità dell'elenco schemi e del certificato di accreditamento rilasciato al PTP.

L'eventuale simbolo (*) indica che è attiva una sospensione dell'accreditamento per la specifica attività riportata a fianco

ACCREDIA
L'ENTE ITALIANO DI ACCREDITAMENTO

Membro degli Accordi di Mutuo Riconoscimento EA, IAF e ILAC
Signatory of EA, IAF and ILAC Mutual Recognition Agreements

CERTIFICATO DI ACCREDITAMENTO
Accreditation Certificate

Accreditamento n° *Accreditation n°* **1362** Rev. **1**

Si dichiara che *We declare that*

European Reference Laboratory for Air Pollution (ERLAP) Air and Climate Unit
Directorate C.Energy,Transport and Climate
Joint Research Centre -European Commission
Sede/Headquarters:
- Via E. Fermi 2749 - 21027 Ispra VA

è conforme ai requisiti della norma: UNI CEI EN ISO/IEC 17025:2005 "Requisiti generali per la competenza dei Laboratori di prova e taratura"

meets the requirements of the standard: EN ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories" standard

quale **Laboratorio di Prova**

as ***Testing Laboratory***

L'accreditamento attesta la competenza tecnica del Laboratorio relativamente allo scopo riportato nelle schede allegate al presente certificato. Le schede possono variare nel tempo. I requisiti gestionali della ISO/IEC 17025:2005 (sezione 4) sono scritti in un linguaggio idoneo all'attività dei Laboratori di Prova, sono conformi ai principi della ISO 9001:2008 ed allineati con i suoi requisiti applicabili.
Il presente certificato non è da ritenersi valido se non accompagnato dalle schede allegate e può essere sospeso o revocato in qualsiasi momento nel caso di inadempienza accertata da parte di ACCREDIA.
La vigenza dell'accreditamento può essere verificata sul sito WEB (www.accredia.it) o richiesta direttamente ai singoli Dipartimenti.

The accreditation certifies the technical competence of the laboratory limited to the scope detailed in the attached Enclosure. The scope may vary in the time. The management system requirements in ISO/IEC 17025:2005 (Section 4) are written in a language relevant to dei Laboratori di Prova operations and meet the principles of ISO 9001:2008 and are aligned with its pertinent requirements.
The present certificate is valid only if associated to the annexed schedule, and can be suspended or withdrawn at any time in the event of non fulfilment as ascertained by ACCREDIA.
The in force status of the accreditation may be checked in the WEB site (www.accredia.it) or on direct request to appointed Department.

Data di 1ª emissione *1st issue date* **2013-06-19**	Data di modifica *Modification date* **2017-05-24**	Data di scadenza *Expiring date* **2021-06-17**
Il Direttore di Dipartimento *The Department Director* (Dott.ssa Silvia Tramontin)	Il Direttore Generale *The General Director* (Dr. Filippo Trifiletti)	Il Presidente *The President* (Ing. Giuseppe Rossi)

Mod. CA-01 rev. 02

Pag. 1 di 1

ACCREDIA
L'ENTE ITALIANO DI ACCREDITAMENTO

European Reference Laboratory for Air Pollution (ERLAP) Air and Climate Unit **Directorate C.Energy,Transport and Climate** **Joint Research Centre -European Commission**	Numero di accreditamento: **1362** Sede **A**
	Revisione: **2** Data: **24/05/2017**
Via E. Fermi 2749 21027 Ispra VA	Scheda **1** di **1** PA1779AR2.pdf

ELENCO PROVE ACCREDITATE - CATEGORIA: 0

Ambient Air

Denominazione della prova / Campi di prova	*Metodo di prova*
Particulate Elemental Carbon (EC) (0.2 to 16 µg/m³)	EN16909:2017
Particulate Matter <10 micrometers (PM10) (3.85 to 150 µg/m3)	EN 12341:2014
Particulate Matter <2.5 micrometers (PM2.5) (3.48 to 120 µg/m3)	EN 12341:2014
Particulate Organic Carbon (OC) (1.8 to 45 µg/m³)	EN16909:2017

Synthetic mixture gas

Denominazione della prova / Campi di prova	*Metodo di prova*
carbon monoxide (0.015-86 mmol/mol)	EN 14626:2012
nitrogen oxides (NO: 1-962 nmol/mol; NO2: 1-261 nmol/mol)	EN 14211:2012
ozone (1-250 nmol/mol)	EN 14625:2012
sulphur dioxide (1-376 nmol/mol)	EN 14212:2012

Legenda
En= norma europea

ACCREDIA
Il Direttore del Dipartimento
(Dott.ssa Silvia Tramontin)
Firmato digitalmente da: Silvia Tramontin
Data:26/05/2017 23:09:46

La decorrenza del presente elenco delle prove accreditate, coincide con la data di revisione del documento, posta in alto a destra.
Non rileva il fatto che la firma digitale sia stata apposta successivamente

End of report

KJ-NA-29898-EN-N

The European Commission's science and knowledge service

Joint Research Centre

JRC Mission

As the science and knowledge service of the European Commission, the Joint Research Centre's mission is to support EU policies with independent evidence throughout the whole policy cycle.

EU Science Hub
ec.europa.eu/jrc

@EU_ScienceHub

EU Science Hub - Joint Research Centre

Joint Research Centre

EU Science Hub

Publications Office
of the European Union

doi:10.2760/659833
ISBN 978-92-76-12334-7